

1973

The synthesis and cationic rearrangements of novel organosulfur and organosilicon systems

Roland Calvin Kippenhan Jr.
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THE SYNTHESIS AND CATIONIC REARRANGEMENTS OF
NOVEL ORGANOSULFUR AND ORGANOSILICON SYSTEMS.

Iowa State University, Ph.D., 1973
Chemistry, organic

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The synthesis and cationic rearrangements of novel
organosulfur and organosilicon systems

by

Roland Calvin Kippenhan, Jr.

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

For the Major Department

Signature was redacted for privacy.

For the Graduate College

Iowa State University
Ames, Iowa

1973

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DEDICATION

To Nancy

PART I. THE SYNTHESIS AND REARRANGEMENTS OF
ORGANOSULFUR SYSTEMS

HISTORICAL

Sulfenium Ions

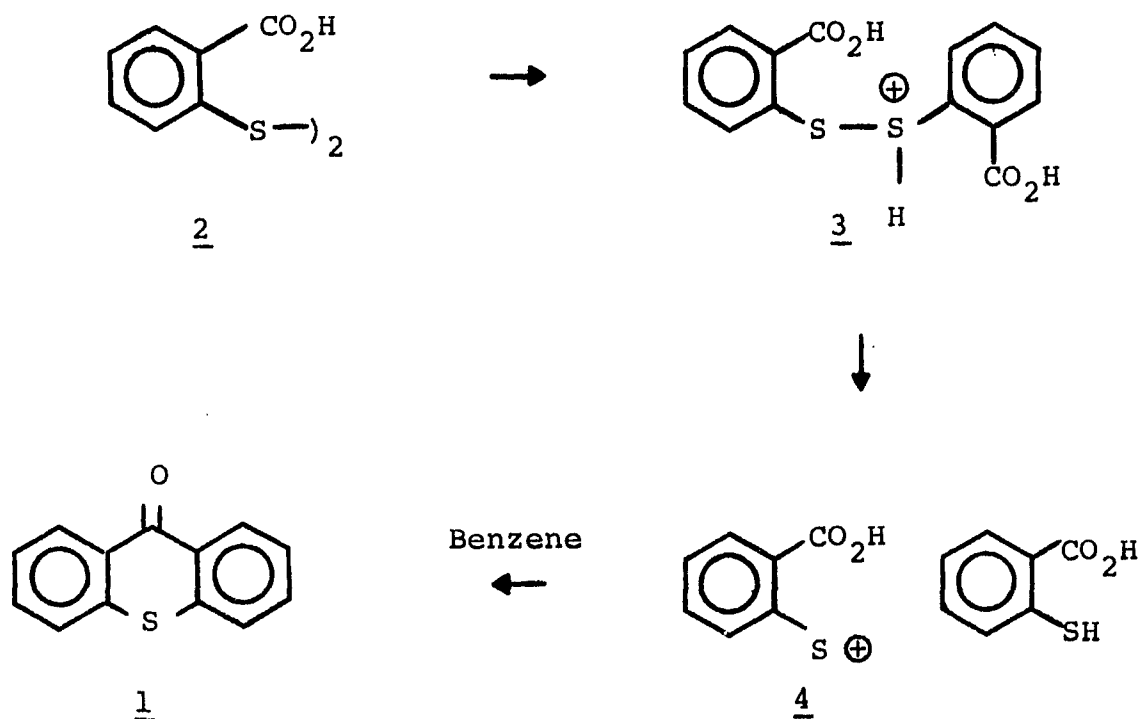
In the history of carbonium ion chemistry distinct stages of development can be recognized. Initially, the trivalent, positively charged carbon atom was proposed as a reactive particle to explain a collection of observations on displacement reactions (1). This was followed by a period of mechanistic work including stereochemical studies, spectroscopic studies, and kinetic measurements in various solvents (2). In the most recent stage of development, properly substituted carbonium ions such as the tropylium ion (3) have been isolated and studied directly.

In contrast to the extensive investigations on carbonium ions, very little was known about the analogous divalent electron deficient nitrogen species until the work of Gassman (4) in 1962. Subsequent work established the nitrenium ion as a useful intermediate resembling a carbonium ion but much more reactive, as would be expected from its greater electronegativity. The electronegativity of sulfur is between that of carbon and nitrogen and one might expect similar behavior for a monovalent, electron deficient sulfur species, to be referred to as the sulfenium ion. Although the sulfenium ion concept has been in the literature for more than a quarter of a century, very little mechanistic work has been done on

the nature of sulfenium ions or their solvated forms.

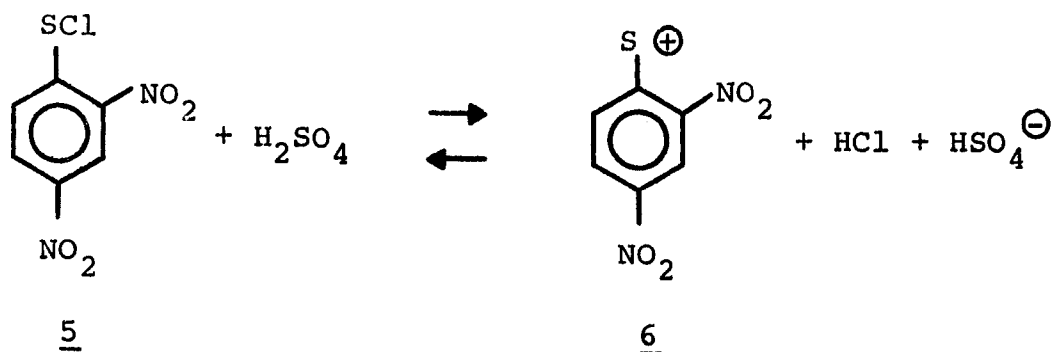
It was first suggested by Foss (5) in 1947 that sulfenic acid derivatives in reactions with nucleophilic reagents eliminate the sulfenyl group as a monovalent cation, RS^{\oplus} . Foss pointed out that a comprehensive study by Kharasch et al. (6) on sulfenic acid derivatives failed to recognize that reactions such as thiosulfonic acid esters, $RSSO_2R$, with cyanide or mercaptide ions might involve the monovalent sulfur cation.

The mechanism of thiaxanthone formation (1) from the condensation of dithiosalicylic acid (2) with benzene was shown by Archer and Suter (7) to involve the protonated dithiosalicylic acid 3.



These authors commented that complete heterolysis of 3 would afford thiosalicylic acid and the ion 4 but were very hesitant to propose that the sulfur cation 4 had even a transitory existence because nothing was known about the behavior of such ions. A transitory existence of RS^{+} was also proposed by Franklin and Lumpkin (8) in electron impact studies with thiols and disulfides.

In 1953 a historic work was published by Kharasch et al. (9) on the interaction of 2,4-dinitrobenzenesulfonyl chloride and sulfuric acid to form a red solution which he ascribed to the positive ion of sulfur and for which he suggested the name 2,4-dinitrobenzenesulfenium ion. Several lines of evidence were presented thereby removing the doubt that earlier workers had about the existence of this species. Kharasch proposed the following equilibrium for the formation of the sulfenium ion.



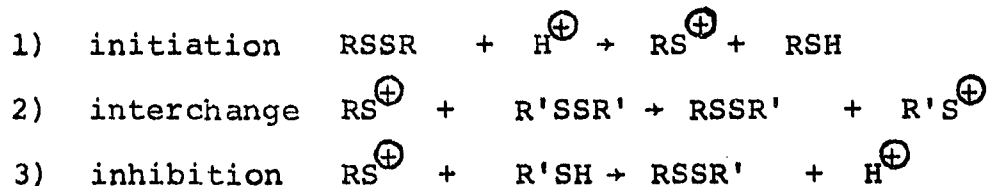
The formation of a bright red solution with the evolution of hydrogen chloride upon dissolution of the yellow sulfenyl chloride 5 pointed to the cleavage of the sulfur-chlorine bond. Addition of bisulfite or dry hydrogen chloride to dilute solutions of 5 in sulfuric acid entirely repressed the development of the red color; this was corroborated by the absorption spectrum, which was characteristic of 6 rather than the red solution of 5 in sulfuric acid. It was found that this red solution could also be generated by treating solutions of 5 in dry ethylene chloride with aluminum chloride or silver perchlorate. Additional evidence was the migration of the red color to the cathode in electrolysis experiments. Cryoscopic measurements were also consistent with a sulfenium ion.

Since the work of Kharasch on the 2,4-dinitrobenzene-sulfenium ion, sulfenium ions have been postulated in many reactions (10). One example of the role of sulfenium ions is found in an investigation of the mechanism of disulfide interchange in acid solution (11),



where the disulfides studied were cystine and bis-DNP cystine. It was found that in neutral or basic solutions the addition of a thiol increased the rate of reaction, but that in acidic

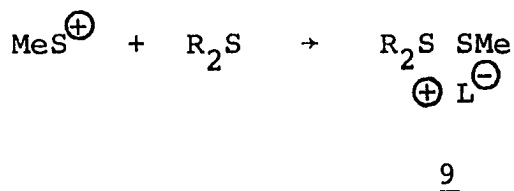
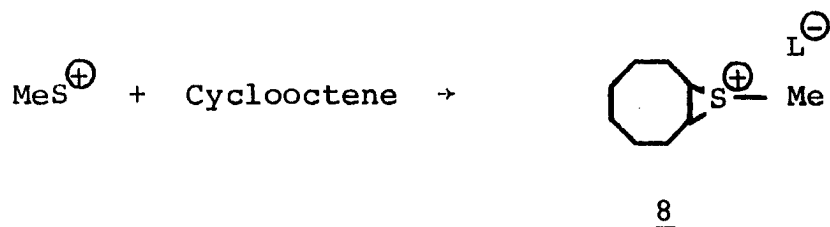
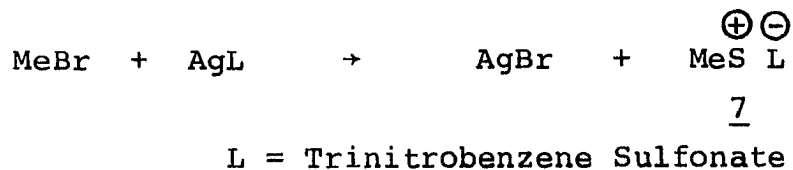
media the addition of thiols suppressed the interchange. This data is consistent with the sulfenium ion mechanism in acid solution, where addition of external thiol would lower the concentration of RS^{\oplus} (Equation 3) and inhibit exchange.



The rate of interchange was extremely sensitive to acid concentration. A number of substances regarded as precursors of sulfenium ions were found to catalyze the reaction including trichloromethanesulfonyl chloride and 2,4-dinitrobenzenesulfonyl chloride.

Only recently have attempts been made to generate sulfenium ions in organic solvents and to use them for synthetic purposes. Helmkamp and Owsley (12) have made use of "methane sulfenium ions" 7 prepared from the reaction of methanesulfenium bromide and silver benzenesulfonate in nitromethane or acetonitrile. The resultant species was trapped by cyclooctene to form an episulfonium salt 8 or by a sulfide to form an alkylated disulfide 9.

The covalency of the sulfur ligand bond is of greatest importance in these investigations. Conductivity studies of the "methane sulfenium ion" indicated an ionic character only when acetonitrile was used as a solvent, and it was suggested



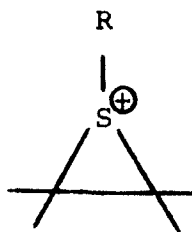
that the ion was coordinated with acetonitrile. In the absence of acetonitrile very low conductivities were observed, suggesting that the bonding is more covalent than ionic. Helmkamp concluded that he was dealing with a sulfenium ion transfer agent rather than a free ionic sulfenium ion. The nmr spectrum in nitromethane showed sharp lines for all protons which was taken as evidence for a singlet state, because a paramagnetic species would have caused line broadening. A chemical shift of δ 2.8 for the methyl protons also was consistent with covalent character. For comparison a methyl group alpha to a carbonium ion in

$\text{HSO}_3\text{F-SbF}_5$ is seen at δ 3.8 (13) and a methyl group alpha to a protonated thiol is observed at δ 3.0 (14).

Owsley and Helmkamp (15) have prepared a benzenesulfenium ion and have obtained evidence of its reaction with molecular nitrogen. Benzenesulfenyl bromide was treated with silver trinitrobenzenesulfonate in a nitrogen stream to isolate a crude impure nitrogen adduct. Elemental analysis and spectral data do show that the nitrogen has been incorporated, but the structure and bonding of this species remains to be determined. Additional evidence for sulfenium ions is found in the addition reactions of sulfenium halides to alkenes and alkynes, presented in the next section.

Addition of Sulfenyl Halides to Alkenes and Alkynes

An examination of the products of the reaction of sulfenyl halides with unsaturated compounds suggests that the initial addition of RS^\oplus is followed by attack of Cl^\ominus and as such might proceed through a carbonium ion intermediate similar to other additions of HX. Early studies (16), however, on β -halo sulfides showed that sulfur has a very strong neighboring group effect. It was suggested that these reactions were different from the additions of HX to olefins in that a discrete intermediate, the thiiranium ion 10 or episulfonium ion was involved (17, 18).



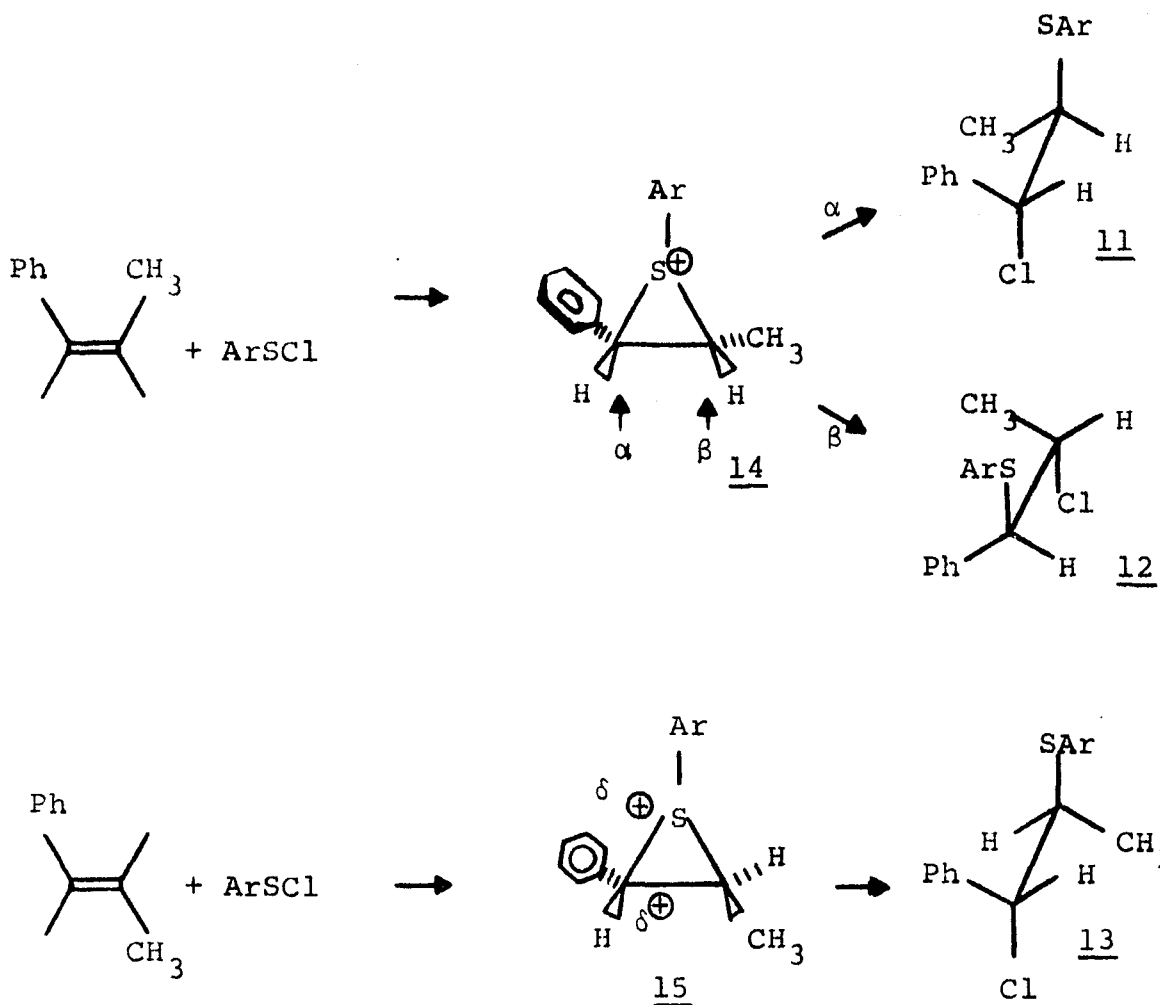
Evidence for the thiiranium ion was obtained in a study of sulfenyl halide additions to cis- and trans-2-butene (19). The products were analyzed and found to result from stereospecific trans addition to the double bond, and argued very strongly against open carbonium ions. Additional evidence for thiiranium ions as intermediates is found in recent studies in which stable crystalline thiiranium salts such as the cyclooctene methylsulfenium ion salt 8 have been isolated (12). A kinetic study of the reactions of aromatic sulfenyl halides with cyclohexene found a rho value of -0.714 when σ^+ constants were used. The correlation with σ^+ constants is consistent with charge development in the transition state and is good evidence for a thiiranium ion (20).

Although the trans mode of addition is well established (21), the orientation of the addition of sulfenyl halides to olefins is a more complicated area. The orientation will be referred to as "Markovnikov" or "anti-Markovnikov" by analogy to additions of HX to olefins. With terminal olefins steric factors are very important in controlling the product

distribution. The kinetic products formed in a study by Mueller and Butler (22) were predominantly anti-Markovnikov with the selectivity increasing with the size of alkyl substituents.

Buess and Kharasch (23) reported that only Markovnikov type products were formed with aryl olefins, but later investigations showed that a post-isomerization was often occurring (21). Kinetic products formed at lower temperatures were missed when the reactions were carried out at room temperature, and only the thermodynamic products were isolated. Phenyl substituents on the olefin, particularly, complicate the mechanism in that ring opening occurs at the benzylic carbon leading to Markovnikov products.

A recent paper by Schmid et al. (24) investigated the problem of mechanism in a careful study of the addition of aromatic sulphenyl chlorides to cis- and trans-1-phenylpropene. Addition to the cis-1-phenylpropene gave only threo-Markovnikov 11 and threo-anti-Markovnikov products 12 while trans gave only the erythro-Markovnikov product 13. This can be contrasted with the additions of bromine and chlorine to 1-phenylpropene which are completely nonstereospecific and involve an open benzylic carbonium ion (25). The difference in orientation of products from cis and trans-isomers can be explained on the basis of steric crowding. The crowding is more severe in the case of the thiiranium ion formed by

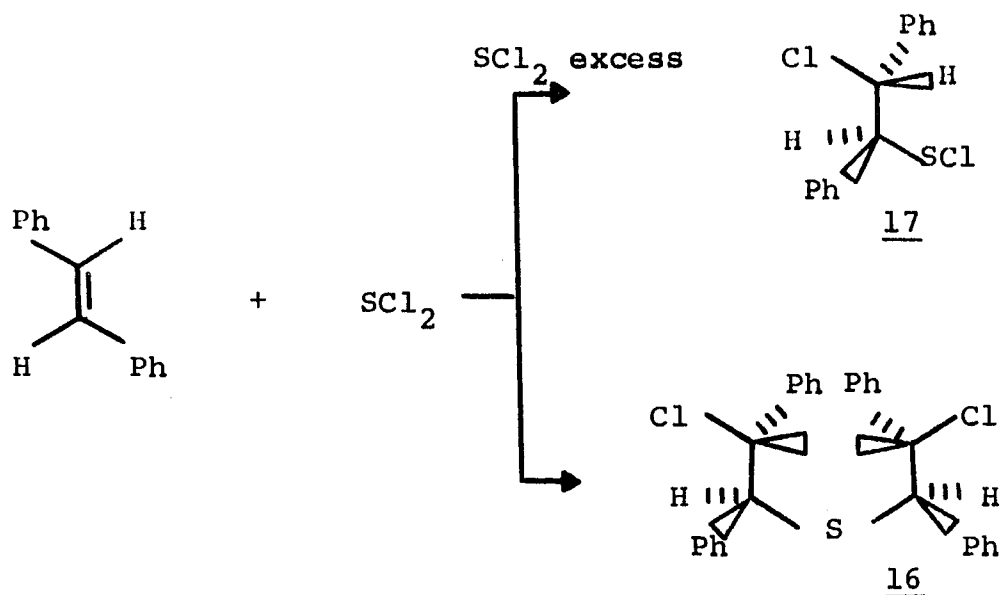


addition to the cis 14 than to the trans olefin 15. The phenyl ring is now unable to rotate to a position such that a positive charge on the benzylic carbon can be stabilized. Therefore, attack on the carbons labelled α or β proceeds through transition states of comparable energy and the mixture of Markovnikov and anti-Markovnikov products is observed. In the case of the trans olefin the transition state for attack at the benzylic carbon is stabilized by the phenyl ring which

is now not restricted in its rotation, resulting in the formation of only the Markovnikov product. This steric crowding also affects the rate determining step in that the trans isomer reacts faster than the cis. Variable temperature nmr studies (26) show that at 146° some interconversion of threo and erythro isomers takes place but suggests that there is a significant difference in activation energy for the formation of the open ion compared to the bridged ion.

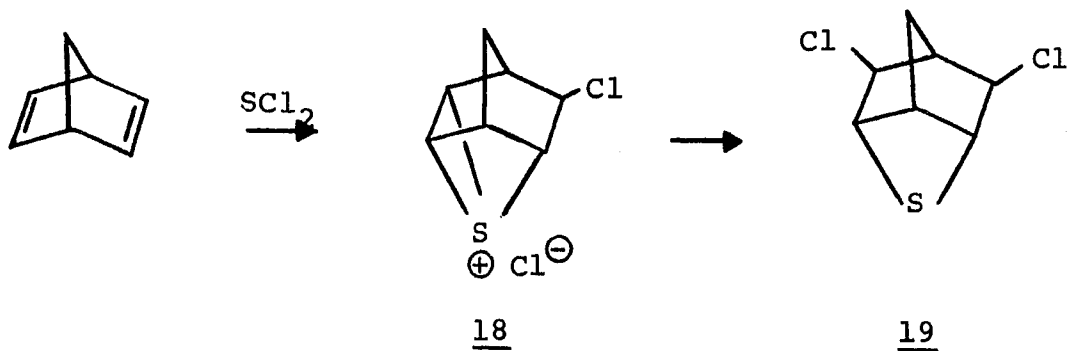
In summary, the thiiranium ion is required in the rate determining step to explain the completely stereospecific reaction. Depending on the nature of the substituents, however, a significant amount of positive charge can reside on the adjacent carbon and will be very important in determining the product distributions.

Sulfur dichloride also undergoes addition to alkenes to form initially a β -chlorosulphenyl chloride (27). The mechanism is assumed to involve a chlorothiiranium ion, but detailed studies have been hampered by the competing reaction in which the sulphenyl chloride adds to another molecule of the alkene to form a β -chloro sulfide. Barton and Zika (28) found that sulfur dichloride and trans-stilbene in methylene chloride formed a 2:1 adduct 16. Using an excess of sulfur dichloride, reaction with trans-stilbene gave the β -chlorosulphenyl chloride 17 in which the stereochemistry is assumed to result from trans addition.



Sulfur dichloride additions to cyclic diolefins have also been investigated in the last five years as routes to novel heterocyclic systems (29). Norbornadiene undergoes endo attack through the endo-thiiranium ion intermediate 18 followed by attack of chloride to give the trans bridged dichloride 19. Similar transition states have been proposed in the transannular addition of sulfur dichloride to 1,4-cyclohexadiene (30) and 1,5-cyclooctadiene (31).

The reaction of sulfur dichloride with a linear diolefin was reported in 1967 by Lautenschlager (32). The size of

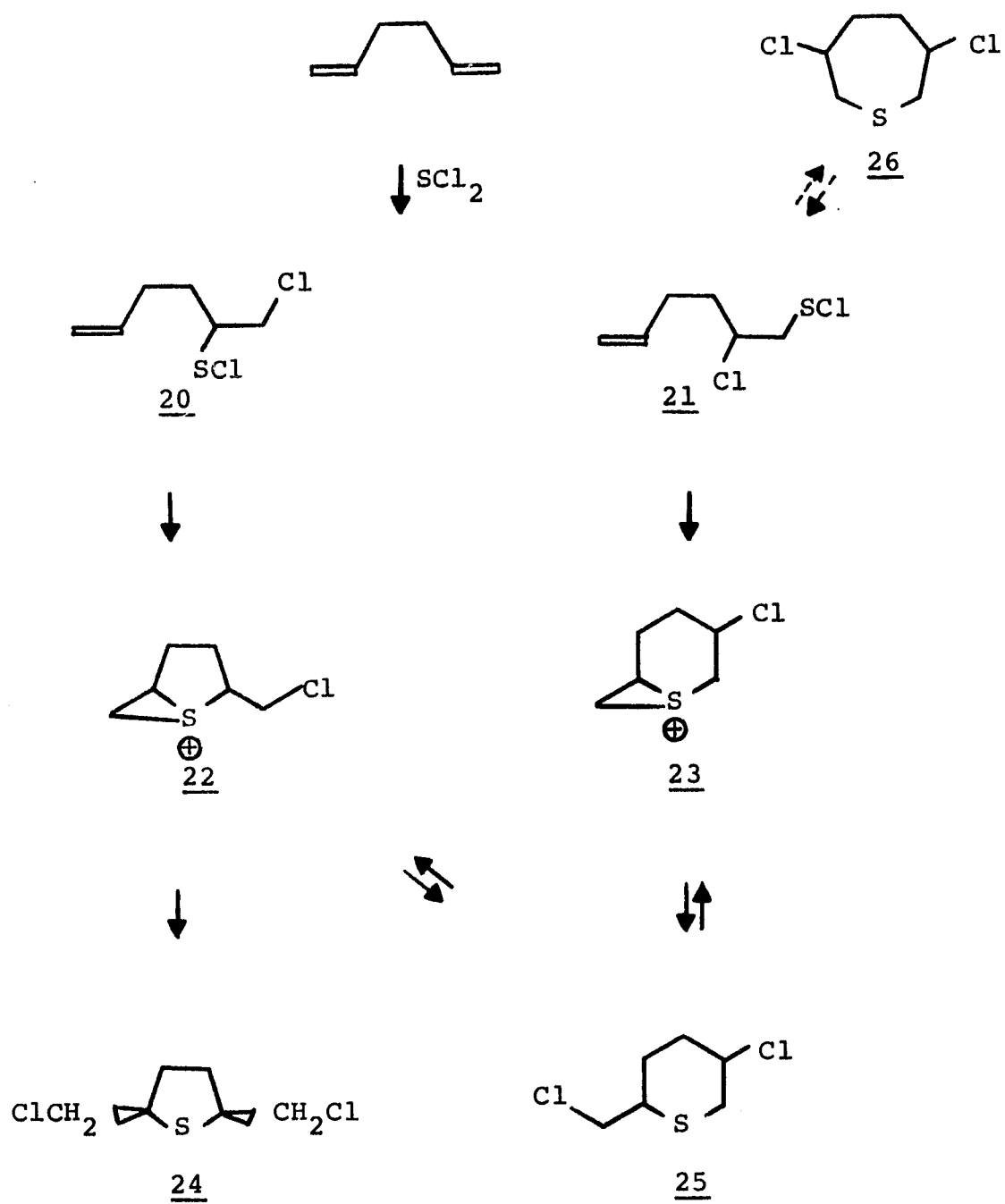


the resulting ring and its stereochemistry could be explained on the basis of thiiranium ion formation and the product determining ring opening mechanism, shown in Scheme 1. The addition of sulfur dichloride to 1,5-hexadiene was expected to proceed through both intermediates 20 and 21. Intra-molecular attack on the second double bond would lead to the intermediates 22 and 23. Chloride attack at the least hindered carbon would then afford the five- and six-membered heterocycles 24 and 25. The cis-five membered heterocycle 24 was the only product isolated in this reaction and was explained by a post-isomerization of 25 through the ion 22 followed by chloride attack at the least hindered site to afford the thermodynamic product 24. No evidence was found, however, for the formation of the pre-isomerized products 25 and 26.

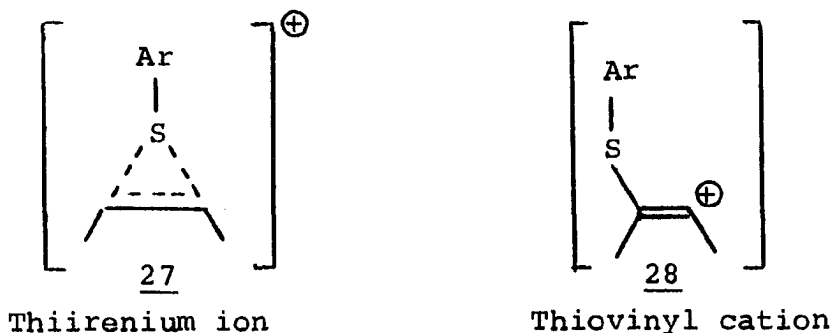
A mechanistic study of the addition of sulfenyl halides to terminal acetylenes was reported by Modena and Scorrano (33), who found only the trans anti-Markovnikov type of addition. The initial study of the electrophilic addition of sulfenyl halides to aryl acetylenes was done by Kharasch and Assony (34) who reported only Markovnikov products. These results were disputed by Calo et al. (35) and also by Schmid and Heinola (36).

Aromatic sulfenyl halides were found to add to acetylenes such as 1-phenyl propyne in an exclusive trans fashion (36).

Scheme 1



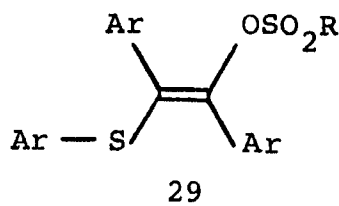
A detailed product analysis showed that the major orientation was Markovnikov, but that the anti-Markovnikov product was also formed. A second order rate expression was found, first order in both the sulfenyl halide and acetylene. The stereospecific nature of addition, by analogy to the reaction with alkenes, implicates the thiirenium ion 27 as an intermediate.



The high Markovnikov/anti-Markovnikov product ratio suggests that the thiirenium ion is not a symmetrical species for aryl acetylenes.

In contrast to the thiiranium ion, no examples of stable thiirenium ions have been isolated and much less is known about their chemistry. Denes et al. (37) have done a theoretical study on the relative stability of the β -thiovinyl cation 28 and the thiirenium ion 27 using a SCF-MO calculation. The bridged thiirenium ion 27 was found to be 65.9 kcal/mole more stable than the linear ion 28 in contrast to protonated acetylenes in which the open cations were more stable than the bridged form by 18.5 kcal/mole.

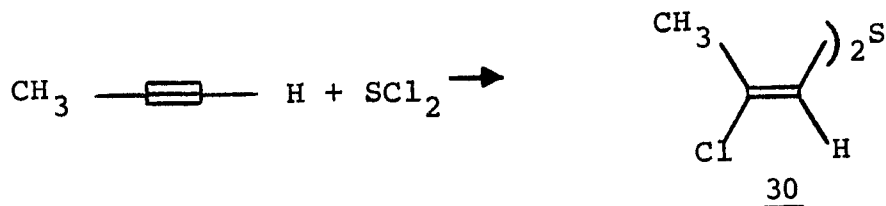
Thiirenium ions have also been postulated as transient intermediates in solvolysis reactions (38). The trans-aryl thiovinyl sulfonate 29 was labelled with ^{14}C at the β carbon and solvolyzed. The isolated products showed that complete ^{14}C scrambling had occurred between the two ethylenic carbons,



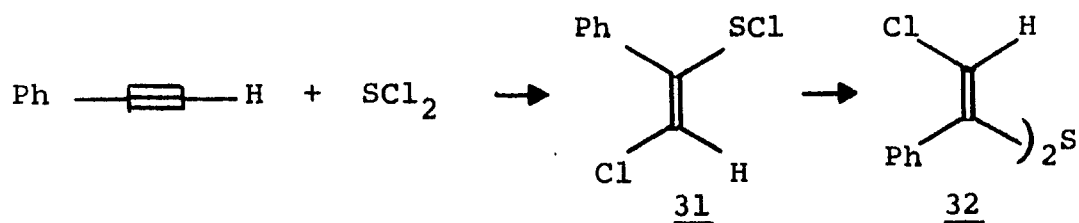
consistent with a thiirenium ion 27.

The precise nature of the thiirenium ion intermediate may vary with the type of substituents and with the solvating power of the medium. A π complex or various ion pairs with differing amounts of covalent character may be involved.

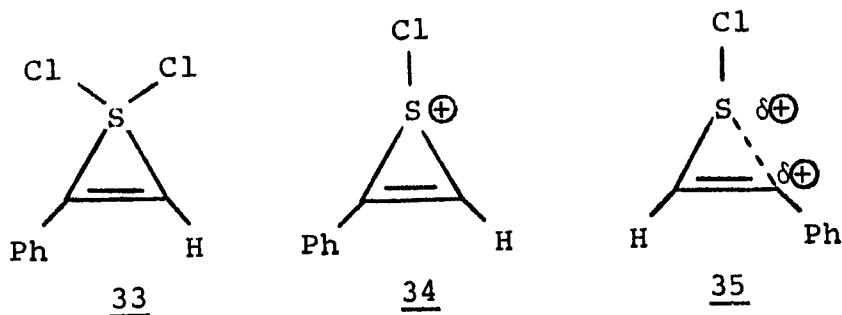
The first report of sulfur dichloride addition to alkynes appeared in 1961 with the work of Brandsma and Arens (39). Addition to an excess of propyne formed the symmetrical divinyl sulfide 30 where no stereochemistry was designated.



Barton and Zika (40) investigated the adducts of acetylenes and sulfur dichloride and found that under certain conditions it was possible to isolate an intermediate vinyl-sulphenyl chloride 31 without formation of the divinyl sulfide



32. The stereochemistry of the reaction was assumed to be trans, and the orientation was mostly anti-Markovnikov. The results were explained on the basis of an initial complex formation which could be either a covalent 33 or ion paired 34 intermediate. Depending on the nature of the substituents

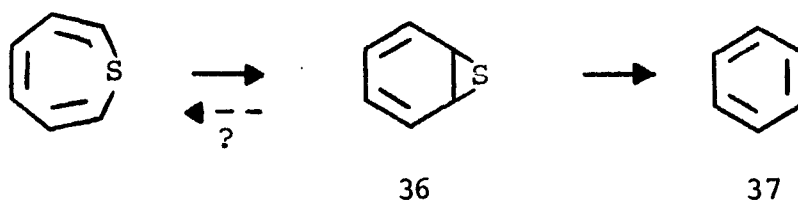


and the solvent an unsymmetrical intermediate 35 was also proposed. These results were surprising in view of the reports of Kharasch and Yiannios (41) that acetylenes are more reactive to sulphenyl halide attack than olefins. Presumably, the low reactivity of the chlorovinylsulphenyl halides is due to deactivation by the electronegative

chlorine group.

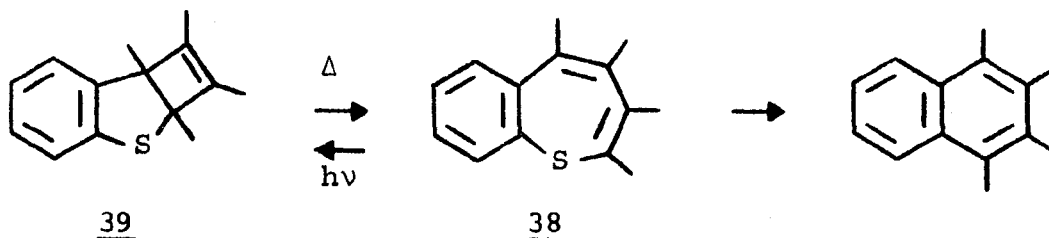
Thiepin

Heterocyclic systems which do not fit the Huckel rule have been a topic of great interest to organic chemists. Seven-membered cyclic 8π systems in which the heteroatom is nitrogen (azepin) and oxygen (oxepin) have been successfully synthesized and quite well studied (42). The sulfur analog (thiepin), however, has been more evasive, and until recently only examples of annulated thiepins were known. In 1972 Dewar and Trinajstić (43) reported MO calculations in which the thiepins were predicted to be antiaromatic. A severe problem in the synthesis of thiepins is the facile extrusion of sulfur which probably occurs from a thianorcaradiene valence isomer 36 to give the corresponding benzene derivative 37 (44).



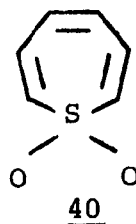
Although benzothiepins have been prepared, the synthetic challenge remains to prepare the unsubstituted annulated systems. The substituents often bias the ring system or prohibit observations to be made on the physical properties

relating to aromaticity or antiaromaticity. The substituted benzo[b]thiepin ring system 38 has been examined by several workers. Neckers et al. (45) found that pyrolysis of a



substituted thiabicyclo[3.2.0]heptadiene derivative 39 afforded substituted naphthalene presumably via the thiepin 38. In 1972 Hofmann and Meyer (46) found that a substituted benzo[b]thiepin could be isolated and that photolysis closed the ring system to the thiabicyclo[3.2.0]heptadiene derivative 39.

Addition of sulfur dioxide to cis-hexatriene, followed by bromination and dehydrohalogenation afforded the first unsubstituted thiepin dioxide (47) 40. The thiepin 1,1-dioxide was found to be very easily hydrogenated and de-



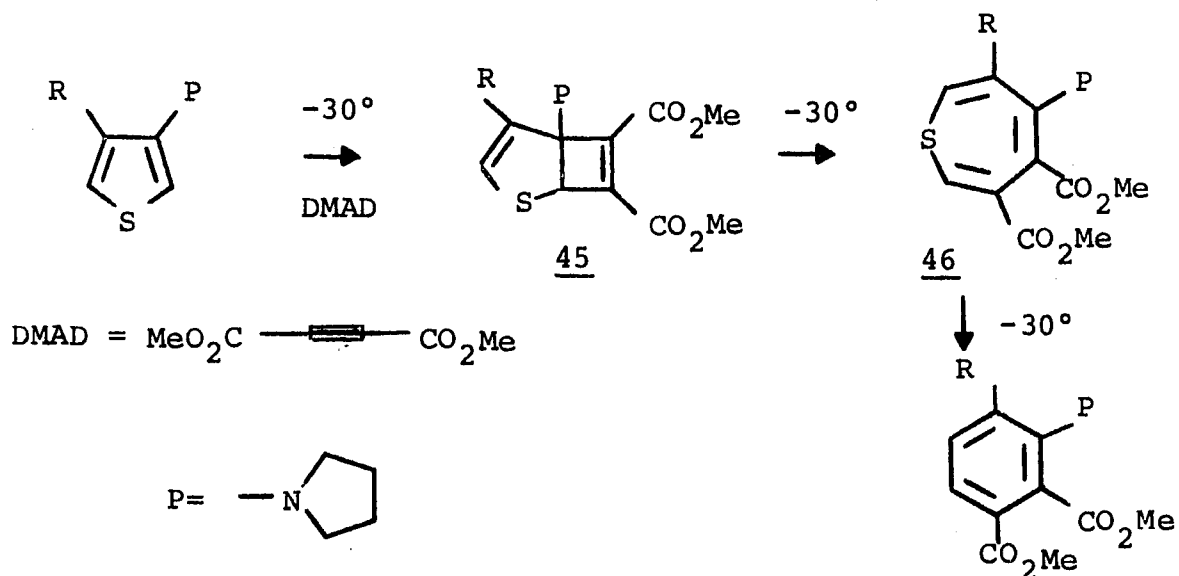
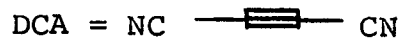
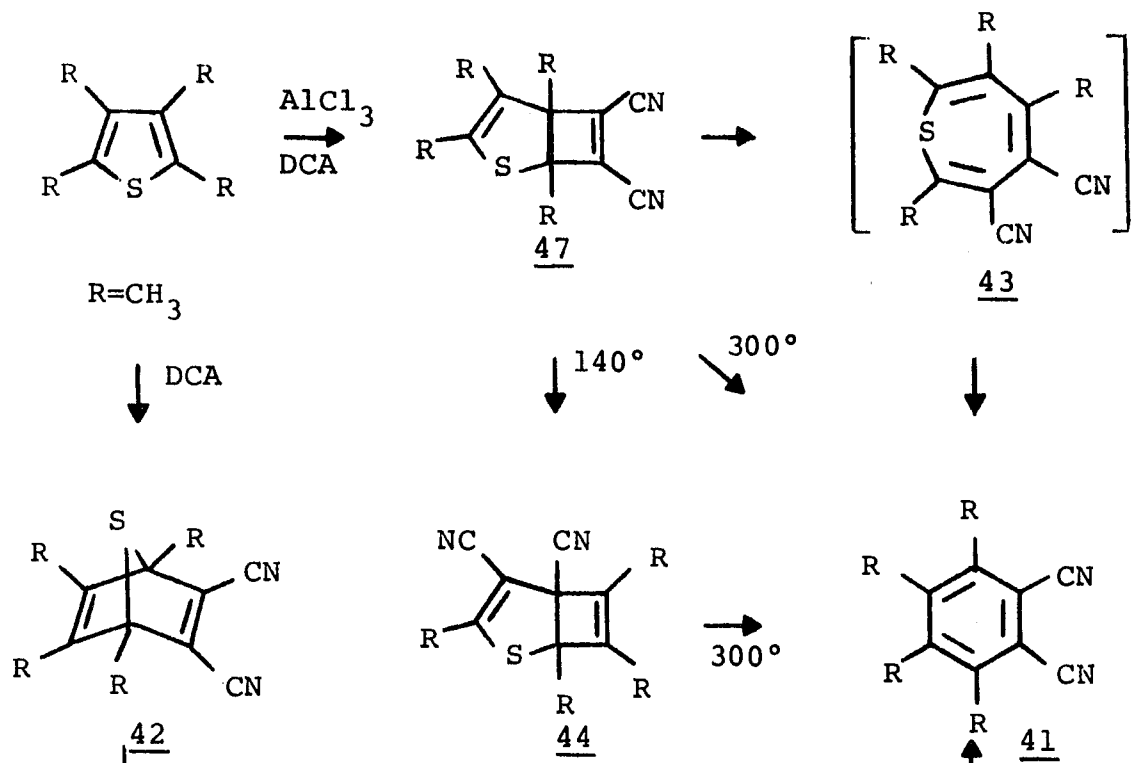
composed at 100° with formation of benzene and sulfur dioxide, indicating a conjugated triene with no benzenoid character.

X-ray studies (48) showed a boat conformation with bond lengths and angles typical of a cyclic polyene, although an nmr study (49) of inversion barriers suggested some conjugation might be present.

The first nonbenzo fused thiepin was prepared by Hoffman and Schlessinger (44), but a dihydrofuran ring was fused to the thiepin and complicated any conclusions on structure and bonding. Barton and co-workers (50) recently reported an attempt to prepare a totally unsubstituted thiepin by dehydrohalogenation of 3,4-dibromo-7-thiabicyclo[4.1.0]heptane. Although the intermediacy of a thiepin was a possibility, only sulfur extrusion products were isolated.

Recently, two groups of Dutch workers independently reported the first synthesis of a mono-cyclic thiepin. Helder and Wynberg (51) found that, contrary to organic textbook statements, thiophenes will undergo Diels-Alder reactions with activated dienophiles, shown in Scheme 2. Tetramethylthiophene reacted with dicyanoacetylene at 60-120° to give tetramethylphthalonitrile 41. A thiabicycloheptadiene 42 was proposed as an intermediate. Using an aluminum chloride catalyst (52), reaction was found to occur at room temperature, and the substituted thiepin 43 was reported. Heating in refluxing xylene gave the thiabicyclo[3.2.0]heptadiene 44 which when pyrolyzed at 300° again extruded sulfur to tetramethylphthalonitrile.

Scheme 2



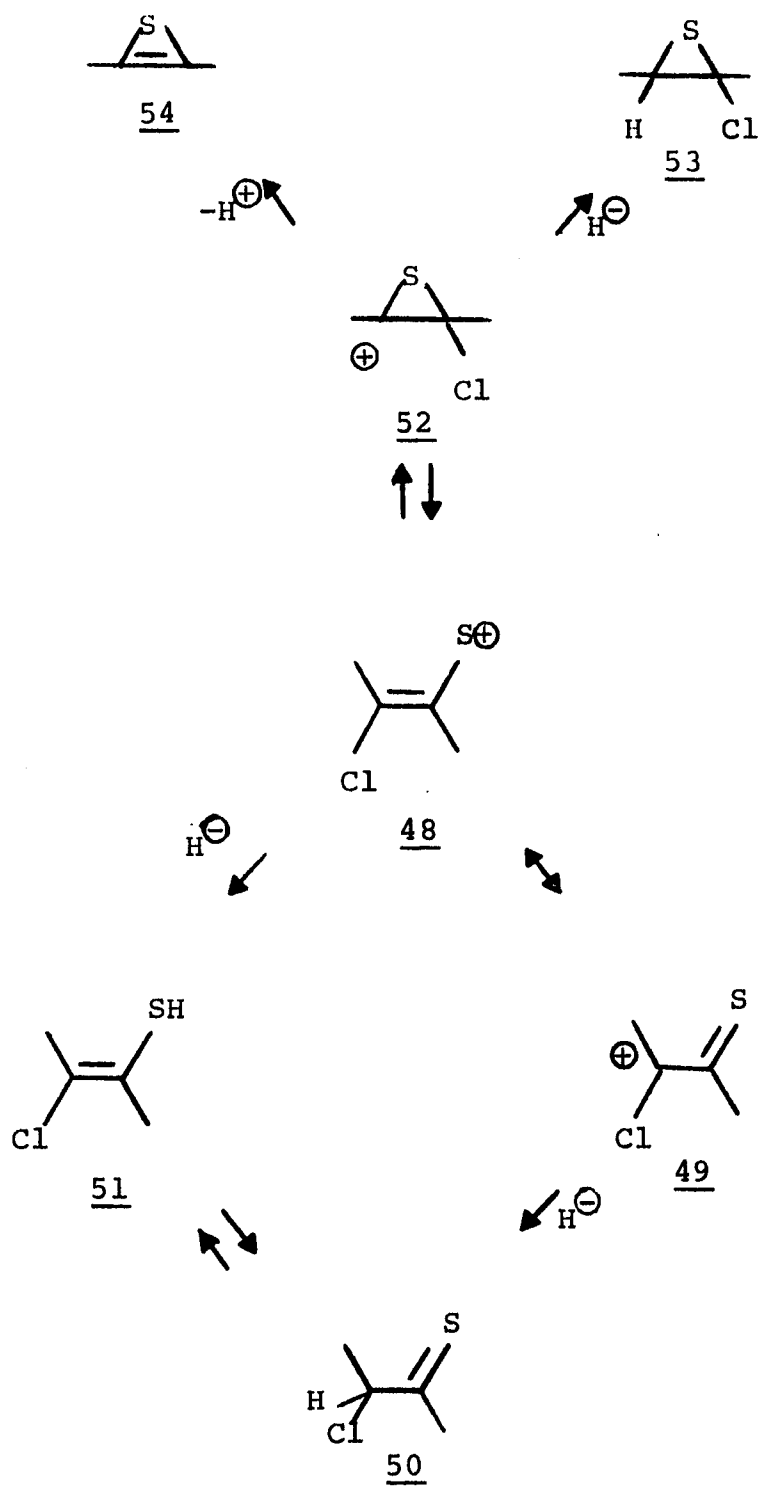
Reinhoudt and Kouwenhoven (53) investigated a cycloaddition of dimethylacetylene dicarboxylate with a pyrrolidinothiophene at -30° by low temperature nmr and ir spectroscopy. The initially formed thiabicyclo[3.2.0]heptadiene 45 rearranged to the thiepin 46 which slowly extruded sulfur at -30° . The difference in stability of thiepins 43 and 46 motivated Reinhoudt *et al.* (54) to reinvestigate the work of Wynberg and Helder. ^{13}C nmr spectra showed that 43 and 44 had the same structural skeleton with two bridgehead sp^2 carbon atoms and the initial adduct was therefore reassigned as 47, instead of the thiepin 43.

RESULTS AND DISCUSSION

Previous workers in organosulfur chemistry sought to generate a stable monovalent, positively charged sulfur species, the sulfenium ion, in order to learn more about the nature of this cation in the chemistry of divalent sulfur. The problem of covalency in these species involving either a nucleophilic counterion or solvent molecules thwarted the success of these attempts. It seemed that a good approach to the problem would employ some nonnucleophilic counterion. A positive charge on sulfur might be further stabilized by an adjacent π center, but this would require the synthesis of a vinylsulfenyl halide as a convenient precursor. Recently a very general route to vinylsulfenyl halides has been reported utilizing sulfur dichloride and various acetylenes (40).

The motivation for generating a vinylsulfenium ion is summarized in Scheme 3. It was expected that the initial ion 48, a hetero allylic carbonium ion, would be stabilized by contributions from the resonance form 49. Hydride transfer was expected to form the thiocarbonyl compound 50 either directly or by tautomerization of the vinyl mercaptan 51. A hydride abstraction by the rearranged cation 52 was considered as a route to thiiranes 53. Another possibility was to use a basic counterion such that a proton loss from the rearranged cation would provide a route to the thiirene ring system (55) 54 which is known only as a transient intermediate.

Scheme 3

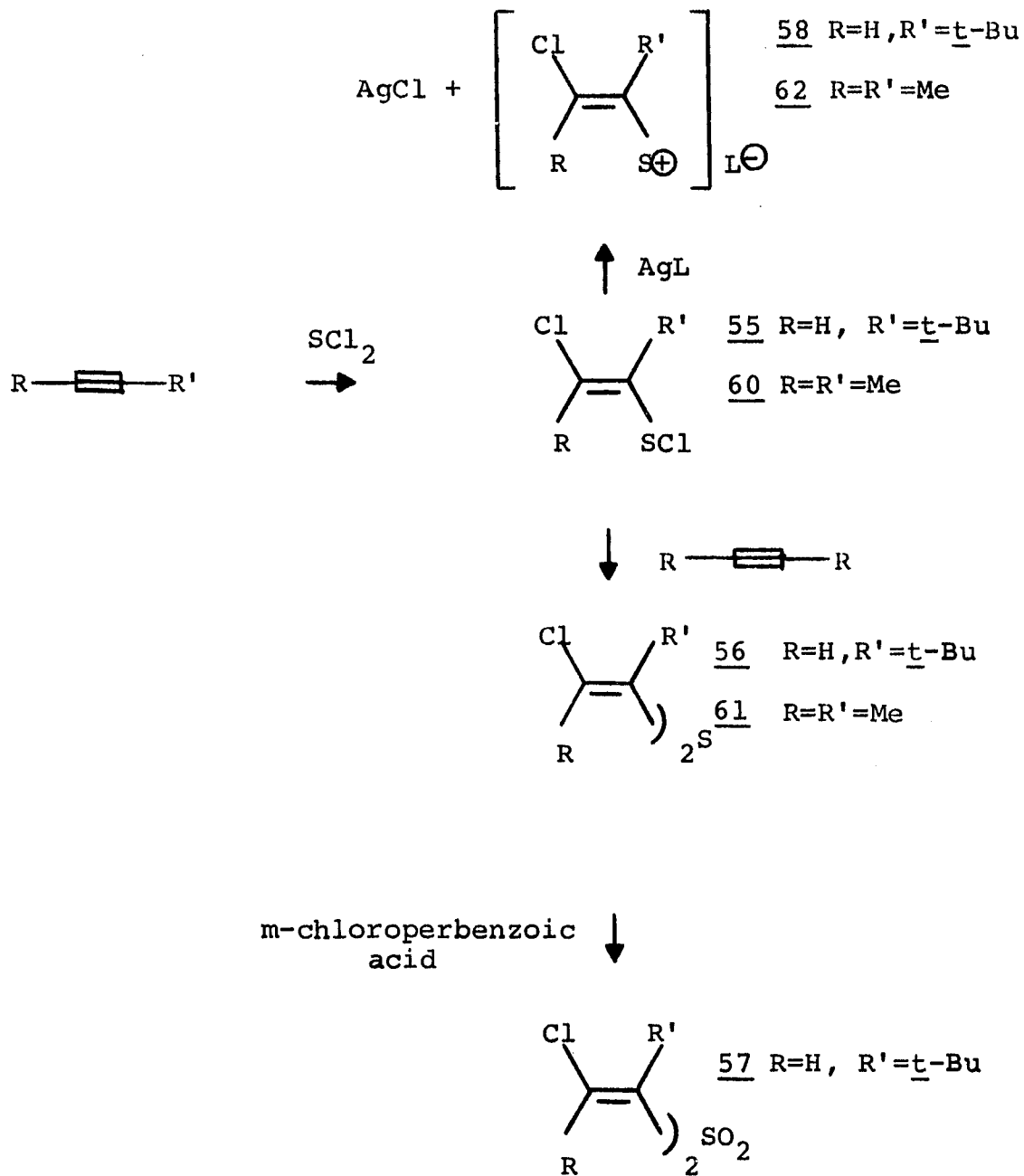


The acetylene chosen for our initial studies was tert-butyl acetylene which added sulfur dichloride under high dilution conditions to afford E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl chloride (55), shown in Scheme 4. The stereochemistry of the products is assumed to be trans and anti-Markovnikov on the basis of the analogous additions of sulfenyl halides to acetylenes outlined in the Historical Section.

The vinylsulfenyl halide was very unstable, and therefore characterization was carried out on bis-E-1-chloro-3,3-dimethyl-but-1-enesulfen-2-yl sulfide (56). Oxidation of the sulfide with m-chloroperbenzoic acid afforded E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl sulfone (57). Complete spectral and microanalytical data were obtained on the sulfone. Evidence that the addition of sulfur dichloride to acetylenes proceeded with the same stereochemistry as additions of sulfenyl halides to acetylenes is seen in the symmetrical nature of the sulfide and sulfone which exhibit only one signal in the nmr spectrum for the two sets of equivalent tertiary butyl protons.

Treatment of the tert-butyl vinylsulfenyl chloride 55 with silver tetrafluoroborate at 0° gave an immediate precipitate of silver chloride which was suggestive of the formation of E-1-chloro-3,3-dimethylbut-1-ene-3-yl sulfenium tetrafluoroborate (58). Studies were then carried out with hydride donors to take advantage of the expected electro-

Scheme 4



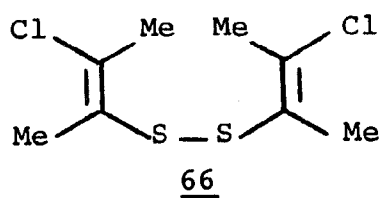
philicity of the positive sulfur, as shown in Scheme 5. The sulfenium ion solution, at 0°, was decanted into a solution of cold cycloheptatriene, and from this reaction a 12.5% yield of tropylium tetrafluoroborate (59) was isolated showing that a hydride ion was definitely removed from cycloheptatriene. An investigation of the hydride acceptor products, however, was thwarted by very complex product mixtures which could not be separated. Extensive investigations to increase the yield of tropylium cation and thereby obtain a cleaner reaction were unsuccessful. Different solvent systems were tried but the sulfenyl chloride was found to react with acetone, benzene, sulfur dioxide, acetonitrile, and dimethyl sulfoxide and limited the use of these solvents. Methylene chloride and nitromethane were also usable solvents but the yields of tropylium cation were no higher than those obtained using ether. A nonterminal acetylene was therefore investigated as an alternative.

Addition of sulfur dichloride to 2-butyne gave E-2-chlorobut-2-enesulfen-3-yl chloride (60) which was characterized by formation of bis-E-2-chlorobut-2-en-3-yl sulfide (61). The reaction of dimethylvinylsulfenyl chloride 60 with silver hexafluorophosphate or silver tetrafluoroborate precipitated silver chloride, showing the generality of the reaction. When E-2-chlorobut-2-ene-3-yl sulfenium hexafluorophosphate or tetrafluoroborate (62) was added to cyclo-

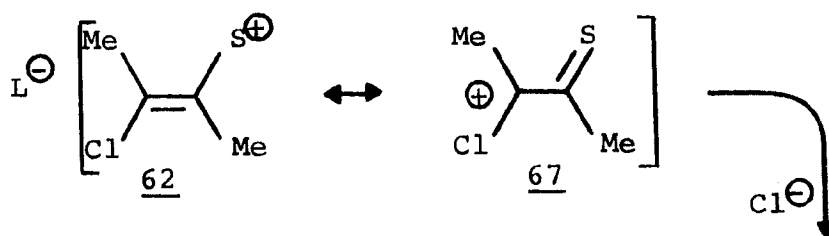
heptatriene, yields of tropylium fluorophosphate (63) or tropylium fluoroborate (59) of up to 48% were determined by nmr analysis. Gas chromatography of the reaction mixture showed the formation of 2-chloro-3-butanone (64) and 2,2-dichloro-3-butanone (65) by comparison with authentic samples. When the same reaction was carried out without cycloheptatriene, bis-E-2-chlorobut-2-en-3-yl disulfide (66) was isolated in good yield. The following mechanism is proposed to explain these observations in Scheme 5. The dimethylvinylsulfenium ion 62 or the resonance contributor or 67 can accept a hydride ion to form the vinyl mercaptan 68 or the thioketone tautomer 69. Hydrolysis of the thioketone 68 in the workup is expected to form the observed 2-chloro-3-butanone (64) on the basis of the well known hydrolysis reactions of thiocarbonyls. The low recovery of any characterizable products is also understandable in light of the known instability of thiocarbonyl compounds (56). Although the instability of thioketones has hampered previous workers, Mayer et al. have reported that the thiocarbonyl-vinyl mercaptan equilibria lies far on the thiocarbonyl side (57).

Formation of 2,2-dichloro-3-butanone in the reaction mixture in a parallel pathway can be explained by chloride attack on 67 to form dichlorothioketone 70, followed by hydrolysis to 65. A mechanism for the formation of the divinyl disulfide 66 is a more challenging question although

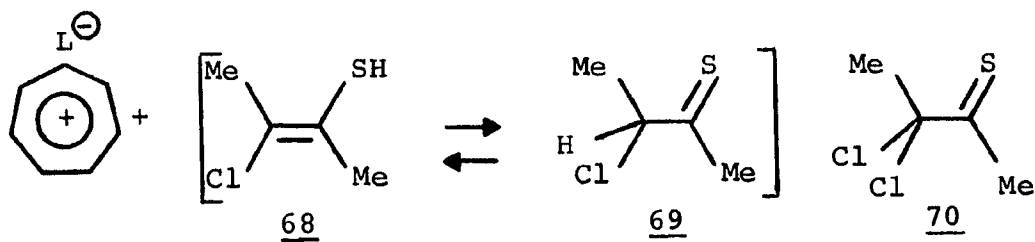
Scheme 5



↑ No Cycloheptatriene



↓ Cycloheptatriene

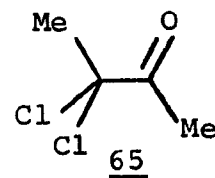
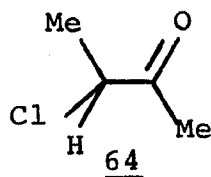


$\text{H}_2\text{O} \downarrow$

$\text{H}_2\text{O} \downarrow$

59 $\text{L}=\text{BF}_4^-$

63 $\text{L}=\text{PF}_6^-$



oxidation of the vinyl mercaptan is one possible pathway. No evidence of any rearranged heterocyclic products was obtained in these reactions.

Substituting silver acetate for silver hexafluorophosphate or silver tetrafluoroborate in the reaction with the dimethylvinylsulfenyl chloride and cycloheptatriene formed no tropylium cation. The competitive pathway was also operative here, and a 27% yield of divinyl disulfide 66 was obtained. The other product isolated and characterized was acetic anhydride. Triphenylmethane was substituted for cycloheptatriene as a hydride donor, but no triphenylmethane cation was detected. Good yields of unreacted triphenylmethane were recovered.

Low temperature nmr studies were carried out in an attempt to observe the sulfenium ion directly. The dimethylvinylsulfenyl chloride 60 was treated with silver tetrafluoroborate at -15° in a nmr tube which was centrifuged (cold) to remove solids and then rapidly transferred to the pre-cooled probe. Only broad lines were observed from δ 1.00 to 3.00, although addition of cycloheptatriene to this solution formed the tropylium cation.

Reactions of arylsulfenyl chlorides with various silver salts were studied in order to determine the relative stability of the dimethylvinylsulfenium ion. A small amount of tropylium cation was isolated when 2,4-dinitrobenzenesulfenyl chloride was treated with silver hexafluorophosphate and cyclohepta-

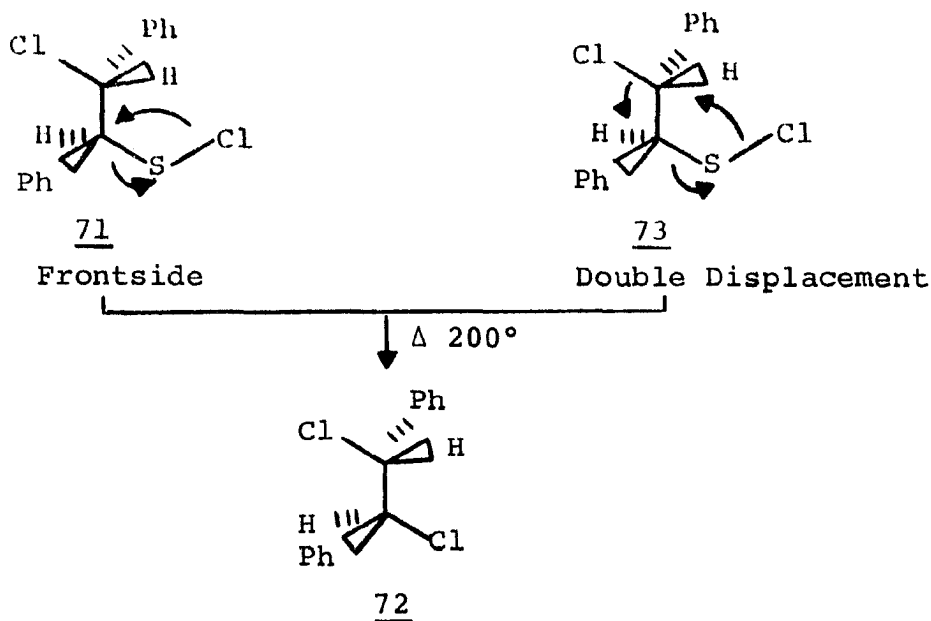
triene. No other products could be identified. The *p*-methoxybenzenesulfonyl chloride was considered as a system in which the electron donating *p*-methoxy substituent would stabilize the corresponding sulfenium ion more than the initially investigated dinitro substituents. Treatment of *p*-methoxybenzenesulfonyl chloride with silver hexafluorophosphate followed by addition of cycloheptatriene resulted in the formation of tropylium hexafluorophosphate. Column chromatography on silica gel cleanly afforded one product which was identified as bis-*p*-methoxybenzene sulfide by comparison with an authentic sample. A more detailed investigation, however, showed that a completely different product was formed prior to chromatography, which lost elemental sulfur on the column. Comparison with authentic samples showed the pre-chromatography product was not a disulfide or trisulfide, but was assumed to be a higher polysulfide. Mass spectrometry showed only the presence of bis-*p*-methoxybenzene sulfide, and all attempts at purification of the pre-chromatography material resulted in loss of sulfur.

It was also desired to prepare 2,4-dimethoxybenzenesulfonyl chloride both by chlorination of the disulfide and the mercaptan. These experiments as well as an attempted trapping experiment with cyclohexene at -10° afforded only a white polymer.

These results prompted a comprehensive literature search

which revealed that 2,4-dimethoxybenzenesulfenyl chloride had never been prepared. In 1964 Mayer and Frey (58) found that the stability of aromatic sulfenyl halides decreased with increasing electron donating substituents on the aromatic ring. For example, p-methoxybenzenesulfenyl chloride decomposed completely in 10 minutes at 90°, whereas nitro substituents greatly hindered decomposition at the same temperature. The products of these decompositions were the corresponding aryl chloride, symmetrical diaryl disulfide and sulfur monochloride. Some aliphatic sulfenyl chlorides were also decomposed to the corresponding alkyl chloride, but yields were reportedly much lower.

Douglass et al. (59) reported that methanesulfenyl chloride thermally decomposed into methyl chloride, methyl-disulfur chloride, methyl disulfide, methyl trisulfide, methyl tetrasulfide, methyl chloromethyl disulfide and dichloromethyl methyl sulfide, and reported that a mechanism of decomposition could not be discerned. Barton and Zika (28) studied the thermal decomposition at 200° of erythro-2-chloro-1,2-diphenylethylsulfenyl chloride (71) and found meso-1,2-dichloro-1,2-diphenylethane (72) and stilbene as major products. Two mechanisms of sulfenyl halide decomposition were then proposed involving either a frontside displacement by the sulfenyl chloride chloride 71 or a novel double backside displacement involving the β -chloro



chloride 73.

In order to determine the mechanism of decomposition of sulfenyl halides, an experiment was designed in which an optically active sulfenyl halide could be obtained with sulfur directly bonded to the asymmetric carbon atom. The commercial availability of optically active 2-octanol prompted a preparation of octanesulfen-2-yl chloride by chlorination of bis-octan-2-yl disulfide. A derivative of the sulfenyl halide was prepared by reaction with cyclohexene for which satisfactory spectral and microanalytical data were obtained. Pyrolysis of octansulfen-2-yl chloride at 450° afforded only the disulfide and no octyl chloride or 2-octene. Higher

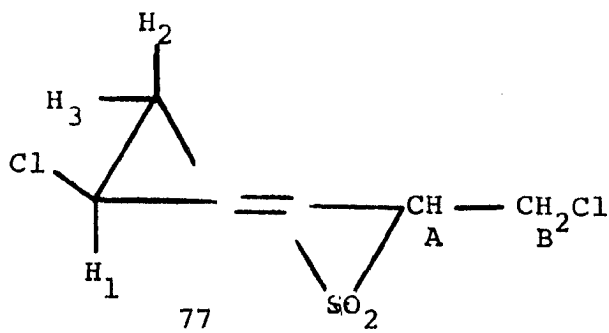
temperatures decreased the yields of bis-octan-2-yl disulfide. At these temperatures, however, the elimination reaction to form 2-octene became the major competing reaction. The small amount of 2-octyl chloride formed in this pyrolysis limited any investigations on an optically active sulfenyl halide, and the nature of sulfenyl halide decompositions remains unknown.

Several investigations on the addition of sulfenyl chlorides to alkyl-substituted terminal olefins have concluded that steric factors control the direction of ring opening of the cyclic thiiranium cation by chloride, thus resulting in anti-Markovnikov products, as outlined in the previous section. However, the product ratio can be drastically changed by the presence of a phenyl group. For example, styrene, which is capable of forming a benzyl cation, affords Markovnikov addition products with greater than 98% selectivity (60). The reaction of *o*-divinylbenzene with sulfur dichloride was investigated in anticipation of forming the cyclic dichlorosulfide 74 which is essentially a double Markovnikov addition product. The dehydrohalogenation of 74 was viewed as a likely route to the unknown benzo[d]thiepin, a molecule for which extensive MO calculations have recently been reported (43).

Under high dilution conditions, simultaneous addition of SCl_2 and *o*-divinylbenzene 75 afforded a 98% yield of an un-

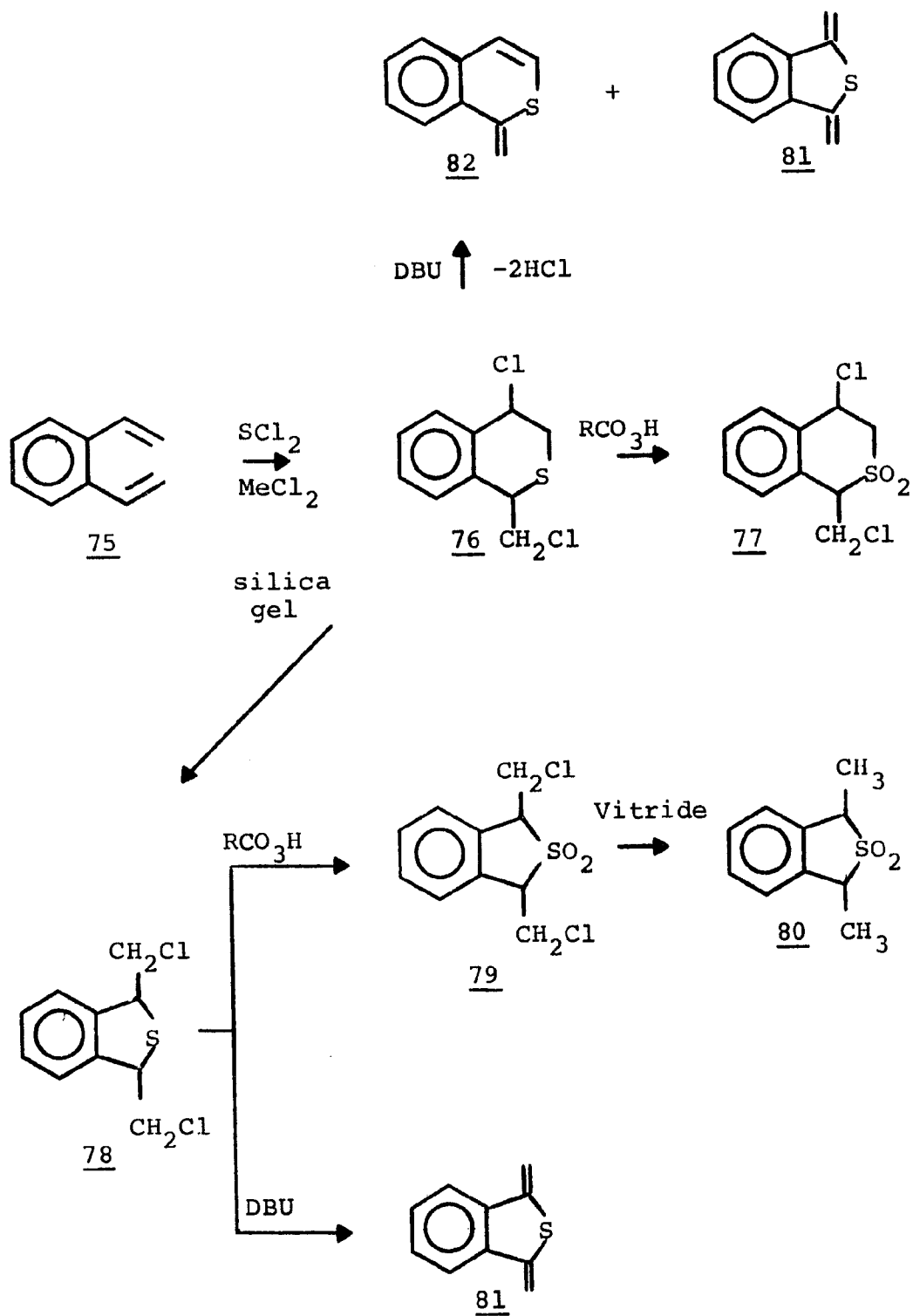
stable product whose complex, unsymmetrical nmr spectrum strongly suggested a mixture of the cis and trans isomers of 1,3,4-H-1-chloromethyl-4-chloro-2-benzothiopyran (76), shown in Scheme 6. Oxidation of 76 with m-chloroperbenzoic acid afforded the sulfone 77 in 90% yield as a mixture of cis and trans isomers from which a single isomer 77a (mp 98-100°) was isolated by fractional recrystallization. The structure of 77a was deduced from nmr analysis (vide infra), facilitated by spin-decoupling experiments summarized in Table 1.

Table 1. Results of spin-decoupling experiments on 1,3,4-H-1-chloromethyl-4-chloro-2-benzothiopyran-2,2-dioxide (77a)



Irradiation Frequency	H ₁ δ 4.85	H ₂ δ 4.40	H ₃ δ 4.15
no irradiation	d of d $\underline{J}_{1,2}=6.6$ Hz $\underline{J}_{1,3}=4.0$ Hz	d of d $\underline{J}_{2,3}=11.5$ Hz $\underline{J}_{1,2}=6.6$ Hz	d of d $\underline{J}_{2,3}=11.5$ Hz $\underline{J}_{1,3}=4.0$ Hz
H ₁ 291 Hz		d $\underline{J}_{2,3}=11.5$ Hz	d $\underline{J}_{2,3}=11.5$ Hz
H ₃ 248 Hz	d $\underline{J}_{1,2}=6.6$ Hz		

Scheme 6



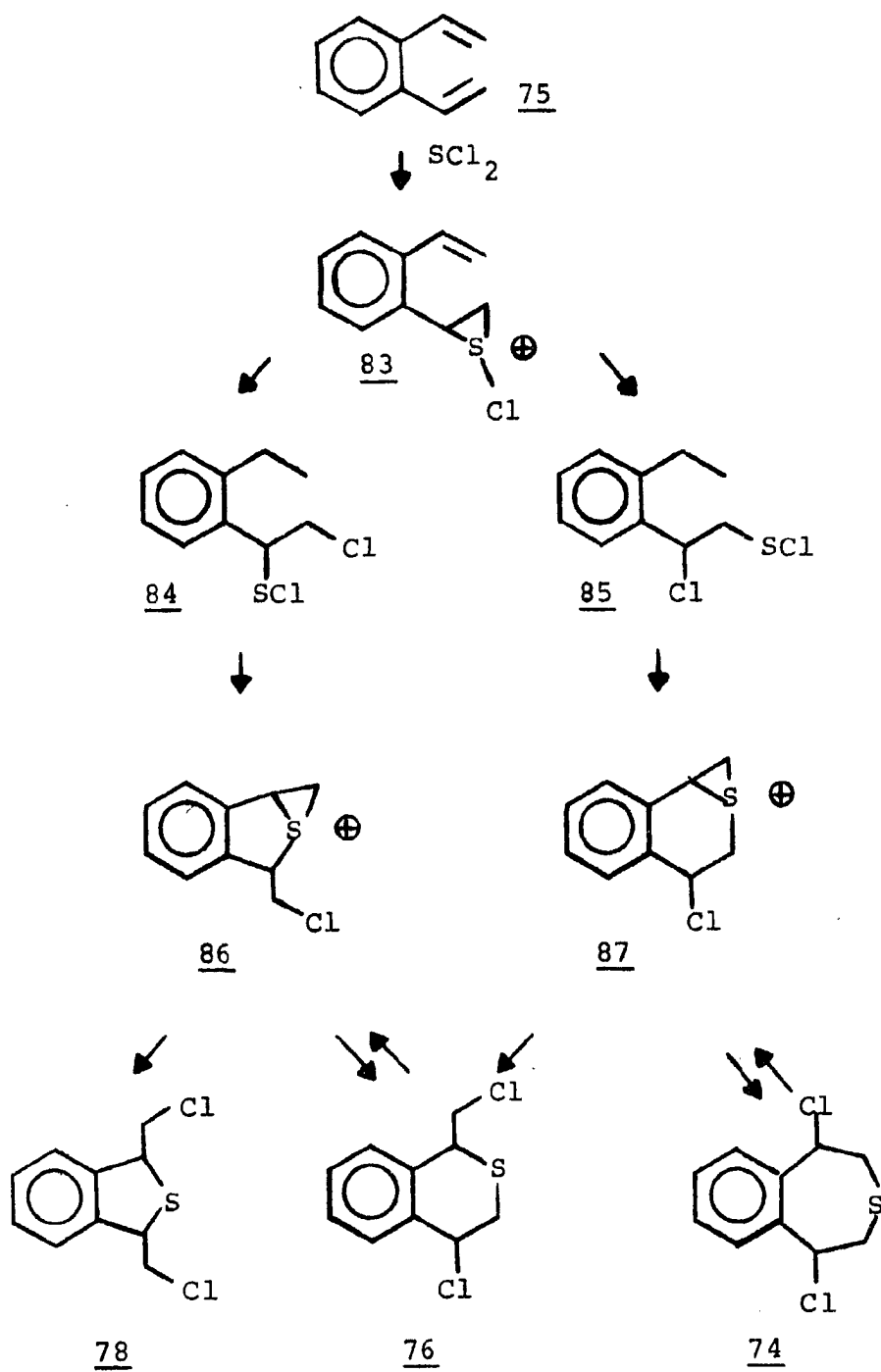
Upon standing at room temperature 76 rearranged to a mixture of 76 and an isomer 78. Complete destruction of 76 was effected by percolation of a solution of 76 through a silica gel column, a procedure which afforded 78 (cis, trans isomer mixture) as the sole isolable product. The nmr spectrum did not by itself allow conclusive differentiation between 78 and 74.

Structure 74 was ruled out through peracid oxidation of 78 to sulfone 79 (85% yield) followed by reductive dechlorination to 80. The nmr spectrum of 80 showed two methyl doublets (δ 1.61 and 1.59, $J = 7$ Hz) thereby eliminating structure 74 from consideration and establishing the dihydrobenzo[c]thiophene system 78 as the rearrangement product from 76.

Additional evidence for the proposed structures was found in the DBU-dehydrochlorination of a mixture of cis- and trans-isomers of 78 to clearly provide only one unsaturated product, 81. While the extreme instability of neat 81 precluded isolation, the nmr spectrum was unambiguous. Similar treatment of 76 with DBU afforded 82 along with 81, the latter presumably arising from partial isomerization of 76 to 78 under the reaction conditions.

A mechanism for this reaction is proposed in Scheme 7 by analogy to the reports by Lautenschlager (32) on the addition of sulfur dichloride to 1,5-hexadiene. Only one

Scheme 7



thiiranium ion 83 can be formed in the initial addition of sulfur dichloride, which can open in two ways to the intermediates 84 and/or 85. The anti-Markovnikov ion 86 can also be attacked in two ways to form a double anti-Markovnikov addition product 78 or the mixed benzothiopyran 76, as a kinetic product. Post-isomerization of the kinetic product 76 through the thiiranium ion 86 would then lead to the observed dihydrobenzo[c]thiophene 78. An alternate pathway is through the mixed thiiranium ion 87 to the benzothiopyran ring system. The same post-isomerization would explain the observed products.

A remarkable finding of this study was the lack of influence of the benzene ring in stabilizing contributions from the open benzylic carbonium ion. The determining thermodynamic factor seems to be the heterocyclic ring size which Lautenschlager established as $5 > 6 > 7$. The isolation of the benzothiopyran 76 contributes to the credibility of this mechanism as well as to the similar mechanism proposed for 1,5-hexadiene, Scheme 1, in which the corresponding intermediate was not found in the reaction mixture. The finding that the six-membered ring sulfide 76 was the initially observed product, therefore, does not rule out the possibility that 74 is the initial product. Indeed the results do not deny the possibility of initial formation of 74 rearrangement to 76 and a slower rearrangement to 78. However, attempts

to observe 74 under quite mild conditions have been uniformly unsuccessful.

EXPERIMENTAL

Infrared spectra (ir) were recorded on a Beckman 12 spectrophotometer. Routine nmr spectra were determined on a Varian model A-60 or a Hitachi R20-B spectrometer, and chemical shifts were reported as parts per million (δ scale) from tetramethyl silane as an internal standard. Decoupling and low temperature studies were recorded on the Hitachi R20-B spectrometer. The Varian HA-100 spectrometer was used to record all 100 MHz spectra. Routine mass spectra were obtained on an Atlas CH-4 spectrometer. High resolution mass spectra were recorded on a MS-902 mass spectrometer manufactured by AEI. Ultraviolet spectra (uv) were recorded using a Cary model 14 spectrophotometer. All melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium, Kronach, West Germany.

E-1-Chloro-3,3-dimethylbut-1-enesulfen-2-yl chloride (55):

A solution of 8.20 g (0.10 mol) of t-butylacetylene in 175 ml of dry methylene chloride was added dropwise to a refluxing solution of 11.30 g (0.11 mol) of freshly distilled sulfur dichloride in 700 ml of methylene chloride. After 2.0 hr of addition time the solvent was removed and the residual red-orange liquid (stench) was distilled at reduced pressure

to give 12.65 g (68.5%) of product: bp 32-34° (0.1 mm);
nmr (CCl_4) δ 1.42 (s, 9H), 7.16 (s, 1H).

Bis-E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl sulfide (56):

To a solution of 3.51 g (19.0 mmol) of E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl chloride (55) in 120 ml of methylene chloride was added 1.58 g (19.2 mmol) of t-butylacetylene in 30 ml of methylene chloride and the resulting solution refluxed for 30 min. After rotary evaporation of ether the residual yellow liquid was distilled at reduced pressure to afford after two distillations 2.80 g (55.1 %) of 56 as a yellow liquid: bp 75-76° (0.13 mm); nmr (CCl_4) δ 1.33 (s, 9H), 6.00 (s, 1H); ir (film) 785, 1360, 1395, 1460, 1475 cm^{-1} ; mass spectrum (70 eV) m/e 266 M^+ .

Bis-E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl sulfone (57):

To a solution of 1.53 g (11.0 mmol) of 85% m-chloroperbenzoic acid in 15 ml of chloroform was added 1.49 g (5.55 mmol) of bis-E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl sulfide (56) in 4 ml chloroform at room temperature. The reaction was exothermic with the temperature increasing to 48°C. After 2 hr m-chlorobenzoic acid was removed by filtration. The filtrates were washed twice with two 30 ml portions of 10% sodium bicarbonate and dried over anhydrous magnesium sulfate. The filtrates were concentrated to afford 1.08 g (64.8%) of white solid. Recrystallization from hexane gave

white prisms of 57: mp 124-125°; nmr (CCl_4) δ 1.44 (s, 9H), 7.44 (s, 1H); ir (KBr) 1570 (m), 1280 (s), 1123 (s), 962 (m), 855 (m), 822 (m) cm^{-1} ; mass spectrum (70 eV) m/e (rel intensity) 300 (3), 298 (8) M^+ , 117 (100).

Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{Cl}_2\text{O}_2\text{S}$: C, 48.16; H, 6.74; Cl, 23.69. Found: C, 48.07; H, 6.78; Cl, 23.52.

E-2-chlorobut-2-enesulfen-3-yl chloride (60):

To a stirred solution of 45.0 g (0.44 mol) of freshly distilled sulfur dichloride in 1-liter of dry ether was added a solution of 12.5 g (0.23 mol) of 2-butyne in 125 ml of dry ether over a period of 4 hr at room temperature. After removal of ether by rotary evaporation the residual red liquid (stench) was purified by trap to trap distillation at room temperature (0.3 mm) to afford 30.9 g (86.0%) of the title compound. The sulfenyl chloride was unstable toward small amounts of acid and moisture. All transfer operations were carried out under nitrogen and the product was stored over sodium carbonate at freezer temperatures: nmr (CDCl_3) δ 2.28 (q, 3H), 2.50 (q, 3H, $J = 1.5$ Hz).

Bis-E-2-chlorobut-2-en-3-yl sulfide (61):

A solution of 2.93 g (18.7 mmol) of E-2-but-2-enesulfen-3-yl chloride (60) in 50 ml of dry methylene chloride was added to a solution of 1.01 g (18.7 mmol) of 2-butyne in 100 ml of methylene chloride over a period of 20 min at room

temperature. After 4 hr the solvent was removed to afford 3.27 g (83.1%) of the title compound which was distilled at reduced pressure: bp 44-46° (0.1 mm); nmr (CCl_4) δ 2.00 (q, 6H), 2.35 (q, 6H); ir (film) 1620, 1375, 1060 cm^{-1} ; mass spectrum (70 eV) m/e 210 M^+ .

Anal. Calcd for $\text{C}_8\text{H}_{12}\text{Cl}_2\text{S}$: C, 45.51; H, 5.73; Cl, 33.58. Found: C, 45.41; H, 5.73; Cl, 33.60.

Reaction of E-1-chloro-3,3-dimethylbut-1-enesulfen-2-yl chloride with silver fluoroborate and cycloheptatriene:

A solution of 1.00 g (5.41 mmol) of E-1-chloro-3,3-dimethyl-but-1-enesulfen-2-yl chloride (55) in 5 ml of dry ether and a suspension of 1.05 g (5.41 mmol) of silver tetrafluoroborate in 5 ml of dry ether were prepared under argon, protected by drying tubes, and cooled to 0°. Addition of the vinyl sulfenyl halide to silver fluoroborate resulted in the immediate formation of a white solid in a yellow solution. The solids were centrifuged to the bottom of the centrifuge tube, and the liquid was decanted into a solution of 0.49 g (5.41 mmol) of cycloheptatriene in 10 ml of ether at 0°.

The solids were dissolved in ammonia then added dropwise to nitric acid to precipitate 0.62 g (80.0%) of silver chloride. The residual ether solution was concentrated to a dark oil from which was isolated 0.120 g (12.5%) of tropylium fluoroborate as an off-white solid by crystallization from ether-hexane. The isolated tropylium fluoroborate was identical to an authentic

sample (61): mp 200° (decomposition); nmr (CD_3CN) δ 9.23 (s).

The experiment was also carried out in nitromethane, and yields of tropylium fluoroborate up to 32% were obtained as determined by nmr. From the residual reaction small amounts of complex product mixtures were obtained which could not be separated by column chromatography.

Reaction of E-2-chlorobut-2-enesulfen-3-yl chloride with silver hexafluorophosphate and cycloheptatriene:

To a solution of 5.40 g (34.4 mmol) of E-2-chlorobut-2-ene-sulfen-3-yl chloride (60) in 25 ml of dry methylene chloride was added at 0° a white suspension of 8.63 g (34.1 mmol) of dry silver fluorophosphate in 20 ml of methylene chloride followed by addition of 3.61 g (34.1 mmol) of cycloheptatriene. All operations were carried out in a nitrogen dry atmosphere (glove bag, P_2O_5). The reaction was allowed to warm to room temperature and was stirred for an additional 5 min.

The methylene chloride insoluble material was triturated with three 20 ml fractions of nitromethane to which was added 150 ml of methylene chloride. Cooling precipitated 1.65 g (20.4%) of white solid tropylium fluorophosphate: mp 250° (decomposition); nmr (CD_3NO_2) δ 9.30 (s); ir (KBr) 1480, 1390, 828 cm^{-1} .

The residual methylene chloride insoluble material was dissolved in ammonium hydroxide, and the silver chloride was

precipitated with nitric acid to afford 3.60 g (73.1%) of white solid.

Column chromatography of the methylene chloride soluble material on silica gel gave 0.072 g (6.9%) of elemental sulfur by elution with pentane: mp 110-113°; no nmr spectrum.

The methylene chloride soluble material was also investigated by vpc analysis. Two major products were identified, isolated by preparative vpc and found to be identical to authentic samples of chlorobutanones (62) as follows: 2-chloro-3-butanone (12.5% internal standard, anisole) was separated on a 10% 6-ft Apiezon L column, column temperature 120°, retention time = 3.8 min: nmr (CCl_4) δ 1.57 (d, 3H), 2.28 (s, 3H), 4.25 (s, 1H); ir (CCl_4) 1710 (s), 1440, 1350 cm^{-1} ; mass spectrum (70 eV) m/e 106 M^+ .

2,2-Dichloro-3-butanone (18.0%) was separated on an Apiezon L column, retention time = 5.0 min: nmr (CCl_4) δ 2.13 (s, 3H), 2.49 (s, 3H); ir (CCl_4) 1720 (s), 1355, 1080 cm^{-1} ; mass spectrum (70 eV) m/e 142 M^+ .

Reaction of E-2-chlorobut-2-enesulfen-3-yl chloride with silver fluoroborate and cycloheptatriene:

To a solution of 4.64 g (30.3 mmol) of E-2-chlorobut-2-enesulfen-3-yl chloride (60) in 50 ml of nitromethane was added at 0° with mechanical stirring a solution of 5.90 g (30.3 mmol) of silver fluoroborate in nitromethane. A solution of 2.80 g (30.3 mmol) of cycloheptatriene in 25 ml of

nitromethane was then added over a period of 5 min. A nmr yield of 48% tropylium fluoroborate was obtained by addition of a known amount of authentic sample. Silver chloride was isolated in the usual way with ammonium hydroxide and nitric acid as a white solid 2.74 g (64%). Analysis by vpc also showed 2-chloro-3-butanone (64) and 2,2-dichloro-3-butanone (65) as described in the previous experiment with silver fluorophosphate.

Bis-E-2-chlorobut-2-en-3-yl disulfide (66):

To a solution of 0.360 g (2.29 mmol) of E-2-chlorobut-2-enesulfen-3-yl chloride (60) in 5 ml of dry ether was added 0.445 g (2.29 mmol) of silver fluoroborate in 5 ml of dry ether at 0° with brief stirring in a centrifuge tube. After allowing the reaction to warm to room temperature the ether insoluble material was removed by centrifugation. The solids were dissolved in ammonium hydroxide, and the silver chloride was precipitated with nitric acid to afford 0.240 g (75.0%) of white solid.

The ether soluble material was chromatographed on silica gel eluting with methylene chloride to afford 0.092 g (30.1%) of the disulfide 66 as a yellow oil: nmr (CCl_4) δ 2.20 (q, 3H), 2.35 (q, 3H); ir (film) 1620, 1435, 1370, 1145, 1095, 1060 cm^{-1} mass spectrum calculated for $\text{C}_8\text{H}_{12}\text{Cl}_2\text{S}_2$ m/e = 241.977577, found m/e = 241.975752.

Low temperature nmr study of the reaction of E-2-chlorobut-2-enesulfen-3-yl chloride with silver tetrafluoroborate:

A nmr tube containing 0.037 g (0.236 mmol) of 2-chlorobut-2-enesulfen-3-yl chloride (60) in 0.3 ml of d_3 -nitromethane was cooled to -15° . A solution of 0.046 g (0.236 mmol) of silver fluoroborate in 0.3 ml of d_3 -nitromethane was then cooled to -15° and added to the sulfenyl chloride solution. After stirring for one minute silver chloride was removed by centrifugation at -15° and the cold tube rapidly transferred to a nmr probe precooled to -15° . The nmr spectrum showed only one broad hump from δ 1.0 to 3.0. A cold solution of 0.022 g (0.238 mmol) of cycloheptatriene was then added, and the tropylium cation absorption was observed in the nmr spectrum: nmr (CD_3NO_2) δ 9.30 (s).

Reaction of E-2-chlorobut-2-enesulfen-3-yl chloride with silver acetate:

A suspension of 1.00 g (6.37 mmol) of silver acetate in 5 ml dry methylene chloride was prepared in a centrifuge tube protected with a calcium sulfate drying tube. After cooling to 0° , a solution of 1.04 g (6.34 mmol) of E-2-chlorobut-2-enesulfen-3-yl chloride (60) in 5 ml of dry methylene chloride was added with magnetic stirring and allowed to warm to room temperature. Centrifugation removed silver chloride which was purified in the usual manner to afford 0.672 g (79.0%) of white solid.

Chromatography on 100 g of silica gel afforded 0.210 g (27.0%) of the bis-E-2-chlorobut-2-en-3-yl disulfide (66) characterized previously: nmr (CCl_4) δ 2.20 (q, 3H), 2.38 (q, 3H).

The methylene chloride soluble material was also investigated by vpc using a 6 ft x 1/4 in. 10% SE-30 column, column temperature = 80° and was found to contain 30.6% acetic anhydride. A preparative sample was collected by vpc and compared with an authentic sample of acetic anhydride: nmr (CCl_4) δ 2.18 (s); ir (film) 1830, 1755, 1370, 1125, 1000 cm^{-1} .

The experiment was repeated with the addition of cycloheptatriene as soon as silver chloride was precipitated. The products isolated were the same, and no tropylium cation signal was observed in the nmr spectrum.

The reaction of E-2-chlorobut-2-enesulfen-3-yl chloride with silver fluorophosphate and triphenylmethane:

To a suspension of 2.00 g (7.90 mmol) silver fluorophosphate in 15 ml dry methylene chloride was added a solution of 1.24 g (7.86 mmol) of E-2-chlorobut-2-enesulfen-3-yl chloride (60) in 5 ml methylene chloride at -10° . A solution of 1.93 g (7.90 mmol) of triphenylmethane in 5 ml methylene chloride was then added and allowed to warm to room temperature. The insoluble material was dissolved in ammonium hydroxide and acidified with nitric acid to afford 0.49 g

(44.1%) of silver chloride. From the methylene chloride was recovered 1.10 g (57.0%) of triphenylmethane: mp 89-91° [lit. (63) mp 94°].

Reaction of 2,4-dinitrobenzenesulfonyl chloride with silver fluorophosphate and cycloheptatriene:

To a suspension of 3.50 g (1.38 mmol) of silver fluorophosphate in 200 ml dry methylene chloride was added a solution of 3.26 g (1.39 mmol) of 2,4-dinitrobenzenesulfonyl chloride in 50 ml methylene chloride at -20° over a period of 10 min. Silver chloride was removed by filtration under nitrogen to afford 1.67 g (85.0%) of silver chloride.

The cold methylene chloride solution was filtrated into 1.28 g (1.39 mmol) of cycloheptatriene cooled to -20° in 50 ml of methylene chloride and allowed to warm to room temperature. A tan solid was removed by filtration and identified as tropylium fluorophosphate in a yield of 0.58 g (17.8%): nmr (CH_3NO_2) δ 9.38 (s).

From the residual black reaction mixture was isolated only small amounts of starting 2,4-dinitrobenzenesulfonyl chloride and cycloheptatriene.

Reaction of p-methoxybenzenesulfonyl chloride with silver fluorophosphate and cycloheptatriene:

To a suspension of 3.70 g (14.3 mmol) of silver hexafluorophosphate in 10 ml of methylene chloride was added a solution of 2.56 g (14.7 mmol) of p-methoxybenzenesulfonyl

chloride in 10 ml methylene chloride at 0°. Silver chloride formed immediately and was followed by addition of 1.32 g (14.3 mmol) of cycloheptatriene in 5 ml of methylene chloride.

After warming to room temperature the methylene chloride insoluble material was removed by centrifugation. The insoluble material was then triturated with 0.5 ml of d_3 -nitromethane and found to contain tropylium hexafluorophosphate: nmr (CD_3NO_2) δ 9.38 (s).

The nitromethane insoluble material was dissolved in ammonium hydroxide then acidified with nitric acid to precipitate silver chloride.

Chromatography of the methylene chloride soluble material on silica gel gave one major product cleanly by nmr which was identical to an authentic sample of bis-p-methoxybenzene sulfide (64): nmr (CCl_4) δ 3.70 (s, 6H), 6.70 and 7.18 (centers AA'BB' aromatic, 8H).

Investigation of the crude reaction mixture revealed that no bis-p-methoxybenzene sulfide was present before chromatography, but rather a different species with the following nmr spectrum (CH_2Cl_2) δ 3.89 (s, 6H) and 7.16 and 7.53 (centers AA'BB' aromatic, 8H). All attempts at purification or characterization of this unknown species by distillation or chromatography resulted in formation of bis-p-methoxybenzene sulfide and elemental sulfur, mp 118-120°.

Bis-p-methoxybenzene sulfide:

The title compound was prepared according to a literature procedure (64). Recrystallization from ethanol gave white prisms: mp 43-44°; nmr (CCl₄) δ 3.72 (s, 6H), 6.70 and 7.18 (centers AA'BB' aromatic 8H).

Bis-p-methoxybenzene sulfone:

To a solution of 1.62 g (8.00 mmol) of m-chloroperbenzoic acid in 15 ml of chloroform was added a solution of 0.92 g (3.76 mmol) of bis-p-methoxybenzene sulfide in 5 ml chloroform as the temperature increased to 50°. The mixture was cooled to 0° after 30 min and m-chlorobenzoic acid was removed by filtration. The chloroform filtrates were washed with 10% sodium carbonate, dried over magnesium sulfate and concentrated to a white solid. Recrystallization from chloroform--hexane afforded prisms, mp 139-140° [lit. (65) mp 139°].

2,4-Dimethoxybenzene thiol:

To a suspension of 4.00 g (0.10 mol) of lithium aluminum hydride in 200 ml dry ether was added a solution of 2,4-dimethoxybenzenesulfonyl chloride in 600 ml dry ether at a rate such that gentle reflux was obtained. After refluxing for 1.5 hr, 40 ml of 1.2 N HCl was added, and the mixture was stirred for an additional 30 min. The ether solution was dried over magnesium sulfate and rotary evaporated to 1.76 g (39.8%) of clear oil: nmr (CCl₄) δ 3.30 (s, 1H),

3.67 (s, 3H), 3.80 (s, 3H), and an aromatic ABX pattern with centers at 6.25 and 7.00 (3H).

Bis-2,4-dimethoxybenzene disulfide:

A solution of 1.76 g (10.3 mmol) of 2,4-dimethoxybenzene thiol in 50 ml of ethanol was treated with 1.50 g (5.93 mmol) of iodine in portions with stirring. After 15 min at room temperature the crude disulfide was collected by filtration and recrystallized from absolute ethanol to afford 0.90 g (51.4%) of white needles: mp 111-112° [lit. (66) 109-112°]; nmr (CDCl₃) δ 3.78 (s, 12H), 6.30-6.50 (m, 4H), 7.35 (m, 2H).

Attempted preparation of 2,4-dimethoxybenzenesulfenyl chloride:

A solution of 0.485 g (1.44 mmol) of 2,4-dimethoxybenzene disulfide in 2.0 ml of chloroform was cooled to -10° and treated with a solution of 0.194 g (1.44 mmol) of sulfuryl chloride in 2.0 ml of chloroform. After warming to room temperature a white solid was collected by filtration. This material did not melt at temperatures up to 250°, was insoluble in nitromethane, acetone, carbon tetrachloride, chloroform and ether and was assumed to be polymeric. The experiment was repeated with cyclohexene present in an attempt to trap the sulfenyl chloride at -10°, but the same insoluble white polymer and unreacted cyclohexene were isolated.

Bis-octan-2-yl disulfide:

To a solution of 4.18 g (28.6 mmol) of 2-octanethiol in 50 ml of absolute ethanol was added iodine in small portions until the iodine color persisted at room temperature. The solution was stirred for 2 hr, concentrated to dryness and the residue dissolved in 50 ml of chloroform. Treatment with a 10% solution of sodium sulfite removed the iodine color. The organic layer was dried over anhydrous potassium carbonate, concentrated and distilled to collect 2.92 g (70.3%) of the desired disulfide: bp 106-108° (0.07 mm), [lit. (67) bp 115° (0.1 mm)]; nmr (CCl_4) δ 2.72 (d, 1H), 0.80 to 1.50 (m, 16H).

Octanesulfen-2-yl chloride:

To a solution of 0.914 g (3.09 mmol) of bis-octan-2-yl disulfide in 10 ml of dry methylene chloride at -20° under nitrogen was added a solution of 0.47 g (3.48 mmol) of sulfuranyl chloride in 2 ml of methylene chloride over a period of 5 min. The reaction was allowed to warm to room temperature for 30 min and concentrated to a yellow liquid. A trap to trap distillation afforded 0.880 g (77.5%) of the desired product: bp 80-85° (1.0 mm); nmr (CCl_4) δ 3.18 (m, 1H), 0.80-1.80 (m, 16H). The product was stored under nitrogen at 0° for use in further experiments.

2-Chlorocyclohexyloctane-2-yl sulfide:

To a solution of 0.237 g (1.31 mmol) of 2-octylsulfenyl chloride in 1.0 ml of dry methylene chloride was added 0.110 g (1.33 mmol) of cyclohexene in 2.0 ml of methylene chloride at room temperature. After 30 min the reaction was concentrated to a clear liquid by rotary evaporation. Distillation at 85-90° (0.1 mm) afforded 0.251 g (72.6%) of colorless liquid: nmr (CCl_4) δ 4.13 (m, 1H), 0.76-2.20 (m, 26H); ir (film) 2835, 2940, 1450, 1465 cm^{-1} .

Anal. Calcd for $\text{C}_{14}\text{H}_{27}\text{ClS}$: C, 63.97; H, 10.35; Cl, 13.49; S, 12.20. Found: C, 63.95; H, 10.23; Cl, 13.40; S, 12.02.

Pyrolysis study of octanesulfen-2-yl chloride:

Pyrolysis studies were carried out at various temperatures using the following general method. The sulfenyl chloride was injected directly into a horizontal pyrolysis oven using a 12 in. Vycor tube packed with glass wool at 10^{-4} mm. The products were trapped at liquid nitrogen temperature. Two of the products were analyzed by vpc by comparison with authentic samples using a 10% carbowax column, column temp = 130°. Retention time for 2-octene = 1.7 min and 2-octyl chloride = 5.2 min. The bis-octan-2-yl disulfide was determined by nmr spectroscopy.

At 450° an overall yield of 48.5% of the disulfide was obtained. Vpc analysis showed no 2-octyl chloride or 2-

octene.

At 480° an overall yield of 36.0% of products was obtained containing 92% 2-octene by nmr and vpc analysis.

At 510° the overall yield was 26.6% of products containing 79% 2-octene and 15% 2-octyl chloride.

1,3,4-H-1-Chloromethyl-4-chloro-2-benzothiopyran (76):

Solutions of o-divinylbenzene (6.90 g, 53 mmol) and freshly distilled sulfur dichloride (5.46 g, 53 mmol) in 125 ml of dry methylene chloride were simultaneously added to 125 ml of stirred methylene chloride. The addition was completed after 1 hr, and the solvent was removed in vacuo to afford 12.0 g (98.2%) of 76 as a yellow oil. Upon standing at room temperature the nmr spectrum revealed that rearrangement to a mixture of 76 and 78 had occurred, thus necessitating the immediate use of 76 in subsequent experiments: nmr (CDCl₃) δ 7.20 (m, 4H), 5.24-5.68 (m, 1H), and 2.80-4.22 (m, 5H); ir (film) 1490, 1445, 1300, 1255, 1025, 770 and 740 cm⁻¹; mass spectrum (70 eV) m/e 232 M⁺.

1,3,4-H-1-Chloromethyl-4-chloro-2-benzothiopyran 2,2-dioxide (77):

To a solution of 76 (2.17 g, 9.3 mmol) in 5 ml of chloroform was added dropwise 3.77 g (18.6 mmol) of 85% m-chloroperbenzoic acid in 50 ml of chloroform over a period of 5 min. After 1 hr, m-chlorobenzoic acid was removed by fil-

tration and the filtrates washed with 10% sodium sulfite until neutral to KI solution. Excess acid was removed by extraction with 5% sodium bicarbonate, and the chloroform layer was dried over magnesium sulfate. Removal of solvent in vacuo afforded 2.0 g (81.9%) of cis- and trans-77 as a colorless oil which solidified upon standing. Repeated recrystallization from chloroform--ether yielded a white solid: mp 98-100°, as one pure isomer 77a : nmr (CDCl₃) δ 3.82 (d, 2H), 5.61 (t, 1H), 4.85 (dd, 1H), 4.19-4.34 (dd, 2H) and 7.50 (s, 4H); ir (KBr) 1140, 1330 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 264 (45) M⁺, 266 (31), 118 (80), 200 (63) 165 (100).

Anal. Calcd for C₁₀H₁₀Cl₂O₂S: C, 45.30; H, 3.80; Cl, 26.74; S, 12.09. Found: C, 45.45; H, 3.99; Cl, 26.75; S, 11.93.

Rearrangement of 1,3,4-H-1-chloromethyl-4-chloro-2-benzothiopyran (76) to 1,3-dihydro-1,3-bis(chloromethyl)benzo[c]-thiophene (78):

Compound 76 (2.3 g) was chromatographed on a 3 x 40 cm column of silica gel with elution by 3 l. of hexane. Concentration in vacuo left 1.47 g (63%) of a red liquid. A small fraction was distilled at 80° (0.1 torr) to afford a colorless liquid for an analytical sample. Both the crude and purified samples had the same isomer ratio and were in all respects identical by nmr. (The ratio of isomers was

approximately 70:30 by nmr, but severe overlap reduces the confidence level of this number.) The purified product darkens rather rapidly and must be stored under nitrogen at 0° in solution. The same conversion was found to occur on neutral alumina. An nmr spectrum of chromatographed material shows no evidence of 76: nmr (CDCl₃) δ 3.82 and 3.84 (2d, 4H), 4.60 and 4.80 (2t, 2H, J = 6 Hz) and 7.20 (sym m, 4H); ir (film) 450, 700, 750, 1435, 1455, 1480 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 232 (6) M⁺, 234 (4); 183 (100), 134 (39).

Anal. Calcd for C₁₀H₁₀Cl₂S: C, 51.55; H, 4.32; Cl, 30.41; S, 13.75. Found: C, 51.74; H, 4.45; Cl, 30.32; S, 13.56.

1,3-Dihydro-1,3-bis(chloromethyl)benzo[c]thiophene 2,2-dioxide (79):

The procedure employed was identical to the oxidation of 76 (vide supra). From 0.410 g (1.76 mmol) of 78 was obtained 0.390 g (85.0%) of yellow oil which was readily crystallized from methylene chloride--ether as a pale yellow solid, 79: mp 117-119°; nmr (CDCl₃) two doublets centered at δ 4.07 and 4.10 (4H), a triplet at 4.60 (2H) and a singlet at 7.49 (4H); ir (KBr) 1490, 1330, 1150, 1120, 730, 540 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 264 (35) M⁺, 266 (24), 200 (100).

1,3-Dihydro-1,3-dimethylbenzo[c]thiophene 2,2-dioxide (80):

To a solution of 79 (0.630 g, 2.4 mmol) in 50 ml of sodium-dried benzene was added 0.80 ml (2.8 mmol) of a 70% benzene solution of Vitride¹ [NaAlH₂(OCH₂CH₂OCH₃)₂] via syringe, and the solution was refluxed for 12 hr. The reaction was cooled to 0° and neutralized with 20% sulfuric acid.

The benzene layer was separated, washed with 10 ml of water, dried over potassium carbonate and concentrated to 0.350 g (72.9%) of 80 as a yellow oil: nmr (CDCl₃) δ 4.22 (q, 2H), 1.61 and 1.59 (two doublets, 6H, J = 7 Hz) and 7.3 (s, 4H); ir (film) 770, 1140, 1320 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 196 (14) M⁺, 132 (100); mass spectrum calculated for C₁₀H₁₂O₂S m/e = 196.055796, found m/e = 196.057587.

1,3-Bis(methylene)benzo[c]thiophene (81):

To a solution of 0.870 g (3.37 mmol) of 78 in 3 ml of acetonitrile was added 1.07 g (7.04 mmol) of 1,5-diazabicyclo-[5.4.0]undec-5-ene (DBU) in 3 ml of acetonitrile, and this solution was stirred for 5 min. The reaction mixture was concentrated to approximately 2 ml; 20 ml of chloroform was added, and the residual acetonitrile and the DBU salts were removed by washing with water. The chloroform layer was

¹Eastman Chemical trademark.

dried over anhydrous potassium carbonate and concentrated under a nitrogen atmosphere. The structure assignment was based on the nmr spectrum since the instability of 81 precluded its purification despite numerous attempts. Oxidation of 81 with m-chloroperbenzoic acid in an attempt to obtain a stable sulfone derivative failed to afford an isolable product. The olefinic protons appeared as sharp peaks at δ 5.24 and 5.78 (each slightly split by geminal coupling, $J = 1$) and the aromatic protons as a symmetrical multiplet at δ 7.50.

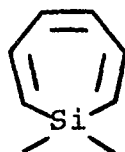
1-Methylene-2-benzothiopyran (82):

The procedure was the same as described above for the reaction of 78 with DBU. The isomeric diolefin 82 was also unstable to isolation, and its structure was based on the appearance of four olefinic peaks at δ 5.15, 5.50, 6.42 and 6.48. The two olefinic peaks of 81 were also observable.

PART II. THE SYNTHESIS AND REARRANGEMENTS OF
ORGANOSILICON SYSTEMS

HISTORICAL
Silepin Synthesis

In contrast to cycloheptatriene, which was obtained by Ladenburg (68) from atropine in 1881, the unsubstituted organo-silicon analog, silepin 88, has not been reported in the literature.

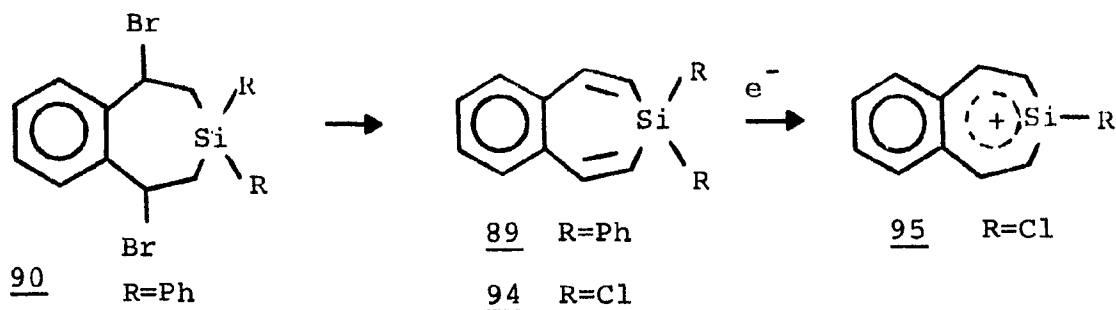


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Extensive work has been invested in the carbon analog of silepin in the past 90 years as summarized in a recent review article by Maier (69). It has been established that cycloheptatriene itself exists in a boat conformation that is rapidly inverting. A coalescence temperature of -140° has been determined at which point the methylene protons show separate signals in the nmr spectrum. As substituents are added to the cycloheptatriene ring system, the inversion barrier increases. This is particularly true for benzo substituents which have been studied for both the carbocyclic and silacyclic systems. Although the geometry of cycloheptatrienes and silacycloheptatrienes are important questions in themselves, there is a unique problem in the silacycloheptatriene ring system. The silicon atom possesses valence shell d orbitals, and as such this system might serve as a probe for

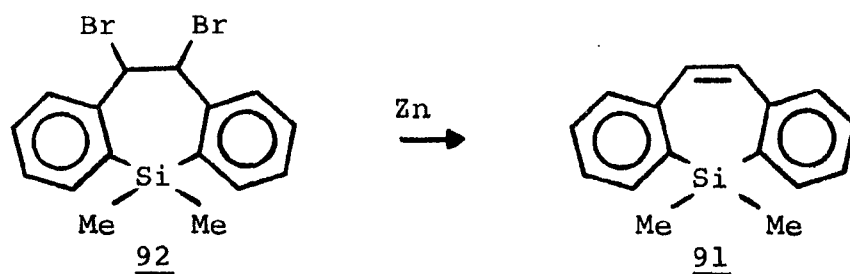
($\pi \rightarrow d$) π bonding. The resulting cyclic delocalization of the 6π electrons might be significant enough to stabilize a planar ring in silepin.

Birkofer and Kramer (70) reported the synthesis of 3,3-diphenyl-3H-benzo[d]silepin (89) by dehydrohalogenation of 1,5-dibromo-3,3-diphenyl-1,2,4,5-tetrahydro-3H-benzo[d]-silepin (90). Very low yields of the desired benzo[d]-silepin 89 were obtained because of the known tendency of the intermediate to undergo the β -halo silicon elimination. The authors concluded that there was interaction between the π electrons through the vacant d orbitals on silicon on the basis of infrared double bond stretching frequencies.



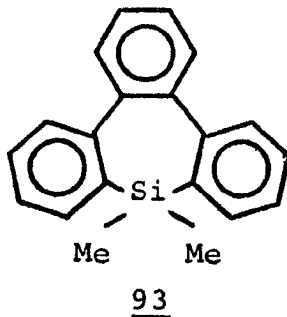
Three groups have independently reported the synthesis of 5,5-dimethyl-5H-dibenzo[b,f]silepin (91) by dehalogenation of the corresponding γ, γ' dibromide 92 (71), by dehydrohalogenation (72), and by dehydrogenation (73). Barton *et al.* (71) have found that the silicon methyl groups of the dibenzo[b,f]silepin 91 appeared as a singlet in the nmr

spectrum at room temperature, which suggested a rapidly inverting boat geometry, a planar geometry or a noninverting boat geometry with fortuitous nmr equivalence of silicon methyl groups. A low temperature nmr study showed no change on cooling until -80° when all lines started to broaden, presumably due to viscosity changes. This observation does not allow a decision to be made on the geometry of the system. The uv spectrum of dibenzo[b,f]silepin 91 was also examined and found to be extremely similar to the all-carbon analog, thus arguing against $(\pi \rightarrow d)\pi$ cyclic delocalization in this system. These authors also noted that the earlier ir spectrum of the benzo[d]silepin reported by Birkofer and Kramer was not significantly different from other vinyl silanes which do not have the possibility of $(\pi \rightarrow d)\pi$ cyclic delocalization.



In 1972 Corey and Corey (74) reported investigations of 9,9-dimethyl-9H-tribenzo[b,d,f]silepin (93), and observed two signals in the nmr spectrum for the two methyl groups at room temperature. At 200° no line broadening was observed,

but a double resonance experiment showed some exchange of sites was occurring. An x-ray structure confirmed the proposed boat conformation of this silepin ring system. These authors pointed out that stereochemical rigidity has also been shown for tribenzo carbon analogs such as 9H-tribenzo[a,c,e]cycloheptene ($\Delta G^\ddagger = 24.0$ kcal/mol at 202°), and that the barriers to rotation for the tribenzo[b,d,f]silepin 93 and the corresponding carbocycles are of the same magnitude.

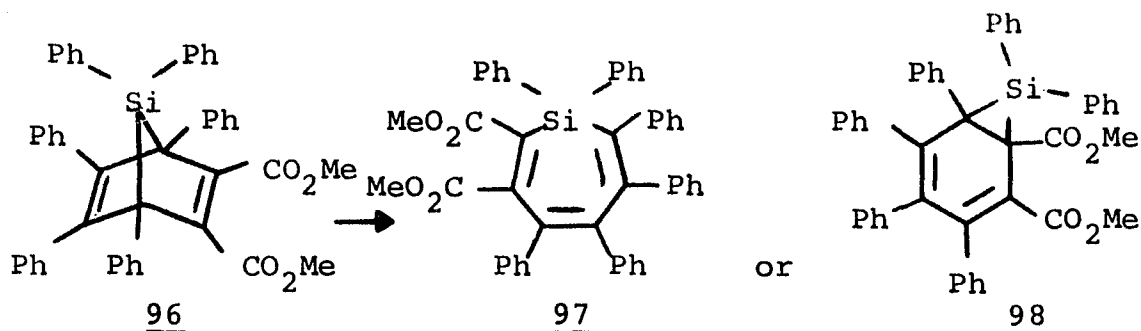


The silepin ring system is also of interest to the heterocyclic chemist as a potential precursor to the silicon analog of the tropylium cation. Surprisingly, there are no examples of the siliconium ion, a trivalent positively charged silicon species. Attempted synthesis of such a species and explanations of the absence of the siliconium ion have been very active areas of research in silicon chemistry. Birkofer et al. (75) have examined the mass spectrum of 3,3-dichloro-3H-benzo[d]silepin (94) and have found a very strong loss of Cl suggesting the formation of a benzosilepinium cation 95.

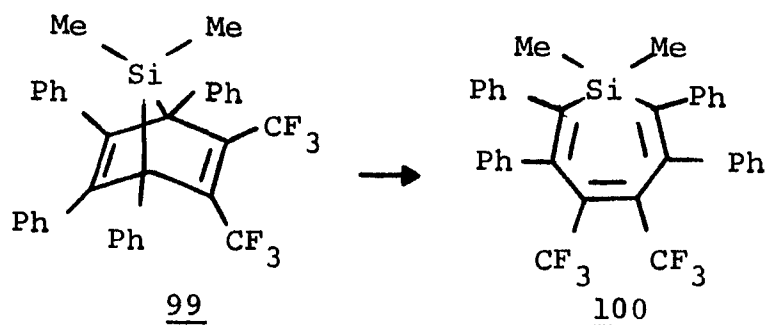
At present, there is no available evidence in support of through conjugation in the silepin system or evidence in support of a planar ring. However, it should be noted that benzosilepins might be poor models in which to look for through conjugation in view of the decreased stability of benzotropylium cations relative to the parent tropylium cation (76). Similar comments can be made on synthetic approaches to a silepinium cation; benzosilepinium cations are expected to be destabilized relative to the parent silepinium cation.

There are several examples of silepins that have tentative structure assignments. Gilman *et al.* (77) reported the reaction of hexaphenyl silole and dimethylacetylene dicarboxylate to form the silanorbornadiene 96. This adduct reacted with ethanol to form a yellow intermediate to which the silepin structure 97 or the norcaradiene structure 98 was tentatively assigned. Decomposition of this intermediate resulted in silylene loss and formation of the corresponding benzene derivative. The complete substitution on this possible silepin system made a positive assignment impossible without x-ray crystallography.

Witiak (78) has investigated the reaction of 2,3,4,5-tetraphenyl-1,1-dimethyl silole and perfluorobutyne. The silanorbornadiene 99 was proposed as an intermediate which



further rearranged to an isomer for which the silepin structure 100 was tentatively assigned.

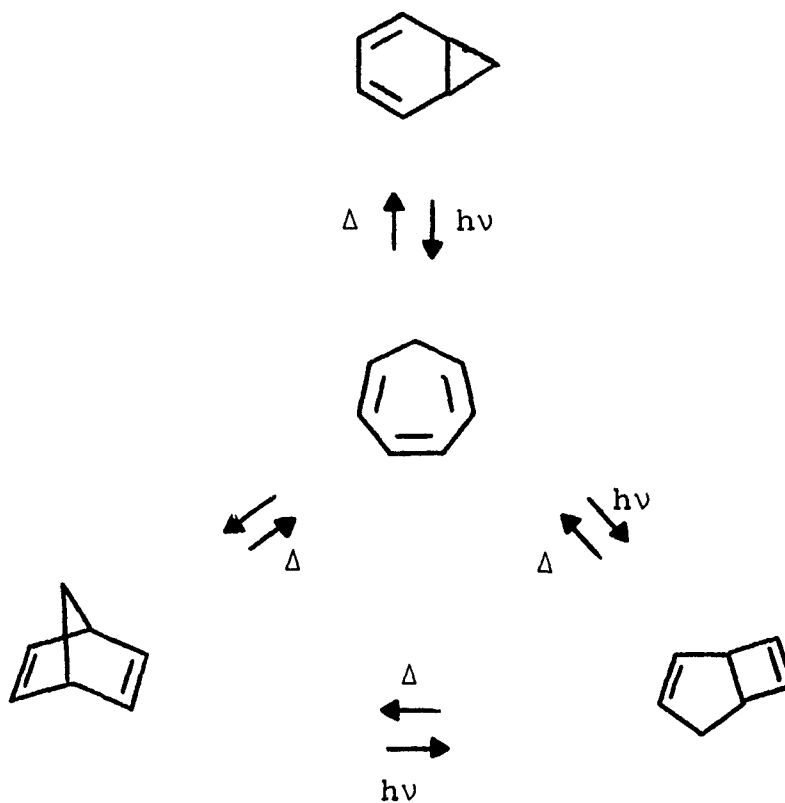


Silepin and Related Carbocyclic Rearrangements

Much of the research effort in the carbocyclic analogs of silepin has been directed toward a study of rearrangements in order to develop better synthetic approaches by a thorough understanding of the rearrangement process, and to explore the implications of orbital symmetry. A brief summary of these rearrangements and their relationship to the silepin problem will be presented in the following section as sum-

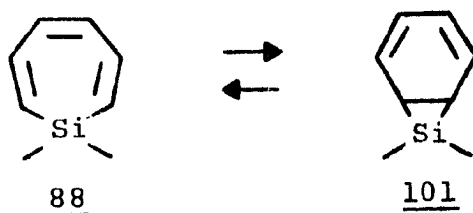
marized in Scheme 8.

Scheme 8



Cycloheptatriene-norcaradiene isomerizations

The thermal isomerization of cycloheptatriene into norcaradiene can be viewed as a disrotatory electrocyclic ring closure and therefore thermally allowed by the rules of Woodward and Hoffmann (79). An important aspect of the silepin problem is to consider the analogous equilibrium between silepin 88 and the silanorcaradiene 101.

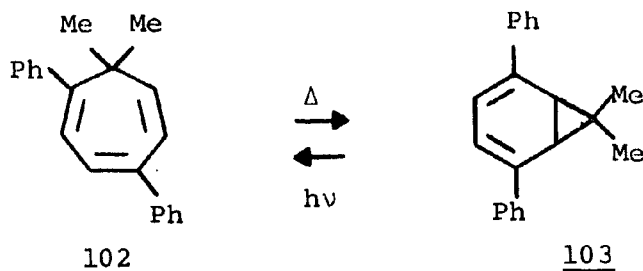


It has been found that simple cycloheptatrienes have equilibria far on the mono-cyclic side, and the norcaradiene structure can be obtained only with π -electron acceptors or in unusual bridging situations (69). This equilibrium is important in the chemistry of other heterocycloheptatrienes. The oxygen analog (oxepin) is known to exist in equilibrium with the oxonorcaradiene, while the sulfur analog (thiepin) equilibrium appears to be irreversible because the thianorcaradiene readily extrudes sulfur to the related benzene derivative (42). A tautomerization of silepin to silanorcaradiene would involve the formation of a silacyclopropane, which with one unusual exception (80) is unknown, and might extrude a divalent silicon to form benzene.

Birkofer et al. (75) pyrolyzed the benzo[d]silepin 94 at 500° and isolated the corresponding hydrocarbon, naphthalene, without comment on the mechanism. Although all reported silepins show no tendency to tautomerize to the silanorcaradiene, it must be pointed out that benzene rings fused in the b, d, or f positions lock the silepin double bonds in the silacycloheptatriene isomer. This question must therefore remain

unanswered until nonannulated silepins can be synthesized.

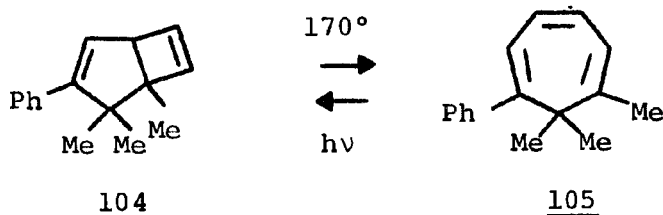
Paquette and Leichter (81) found that pyrolysis of 1,1-dimethyl-2,5-diphenylcycloheptatriene (102) at 200° afforded 7,7-dimethyl-2,5-diphenylnorcaradiene (103). Photolysis of the norcaradiene through Pyrex resulted in a photo-1,5-sigmatropic carbon rearrangement back to the cycloheptatriene. Each of the individual paths have precedence in the literature, but this is the first example of a "closed loop reaction sequence" within the norcaradiene-cycloheptatriene series.



Cycloheptatriene-bicycloheptadiene isomerizations

The isomerization of cycloheptatriene to bicyclo[3.2.0]-heptadiene is a disrotatory $4 e^-$ electrocyclic ring closure and is therefore predicted to be photochemically allowed by the rules of Woodward and Hoffmann (79). In fact, photolysis of cycloheptatriene takes place, but very slowly. Similarly, thermolysis of bicyclo[3.2.0]heptadiene is a forbidden process and is not expected to proceed very readily. In spite of the orbital symmetry imposed barrier, successful pyrolysis of

bicyclo[3.2.0]heptadienes have been accomplished at high temperatures. Paquette and Leichter (81) reported that pyrolysis of bicyclo[3.2.0]heptadiene 104 at 170° afforded 1,1,2-trimethyl-7-phenylcycloheptatriene (105) which could be reversed very cleanly by photolysis through quartz.



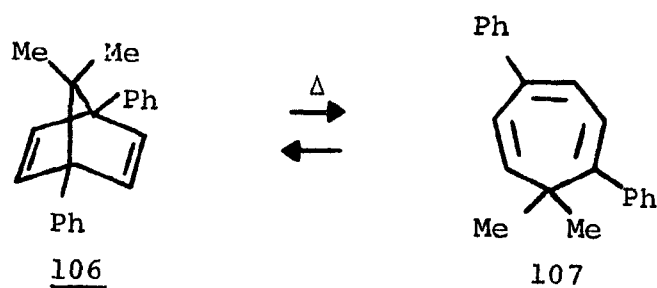
Similar routes have been employed in the synthesis of heterocyclic compounds. Both the synthesis of thiepins (42) and azepins (82) have been reported by pyrolysis of the appropriate hetero bicyclo[3.2.0]heptadiene.

Another convenient route to cycloheptatriene was reported by Dryden (83) in 1954. Solvolysis of bicyclo[3.2.0]-hept-2-ene-6-yl tosylate in acetic acid buffered with sodium acetate afforded cycloheptatriene in an overall yield of 50%. No mechanism was presented, but the allylcarbiny l ion was presumably formed, followed by elimination.

Cycloheptatriene-norbornadiene isomerizations

The thermal rearrangement of 7,7-dimethyl-1,4-diphenyl-norbornadiene 106 was also reported as a route to 1,1-

dimethyl-2,5-diphenylcycloheptatriene 107, presumably via a 1,3 shift with inversion at the migrating center followed by isomerization of the intermediate (not isolated) norcaradiene. The cycloheptatriene 107, however, was a kinetic product and was difficult to isolate. A competing rearrangement also occurred from which the more stable norcaradiene 101 was isolated (81).



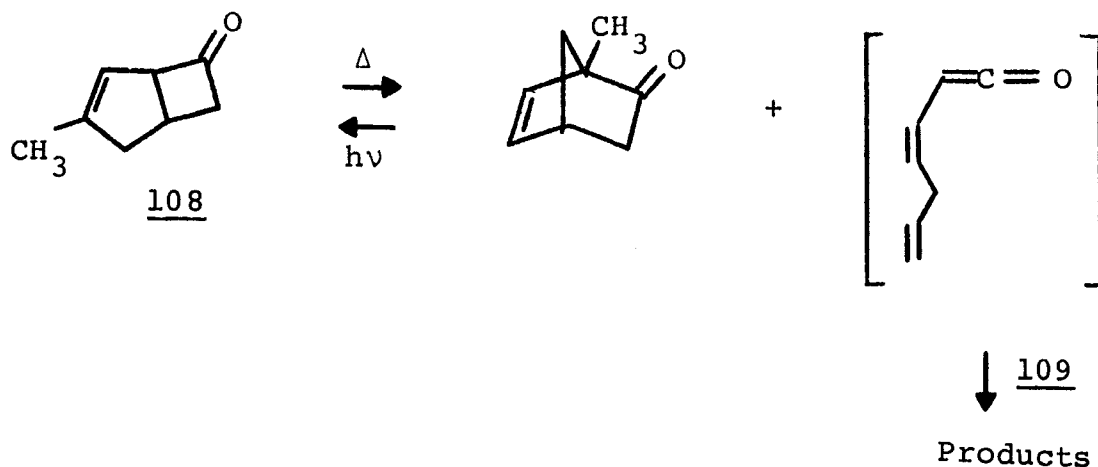
There is possibly a precedence for this type of rearrangement in organosilicon chemistry in the previously mentioned work of Gilman et al. (77). 7-Silanorbornadiene 96 was found to be unstable in methanol and rearranged to silepin, presumably via the same mechanism as presented for the carbon analog.

Norbornadiene-bicycloheptatriene isomerizations

There is another potential relationship between the cycloheptatriene isomers that also deserves to be mentioned. Berson (84) has found that bicyclo[3.2.0]heptenes can be

converted to the appropriate norbornenes by a 1,3 shift with inversion at the migrating center. These findings are related to recent work reported by Russell and Schmitt (85) in which esr studies showed an isomerization between norbornadiene and bicyclo[3.2.0]heptadiene semidiones.

Vapor phase pyrolytic rearrangements of bicyclic systems have been reported by Schiess and Funfschilling (86) who prepared 2-methylbicyclo[3.2.0]hept-2-ene-7-one (108). Pyrolysis at 450° afforded products derived from the ketene 109 formed by a 2 + 2 cycloreversion. Another product isolated was the rearranged isomer, 1-methylbicyclo[2.2.1]hept-5-ene-2-one. The norbornene was cleanly converted to the bicyclo[3.2.0] 108 system by photolysis. No cycloreversion with fragmentation to ketene and methylcyclopentadiene was observed.



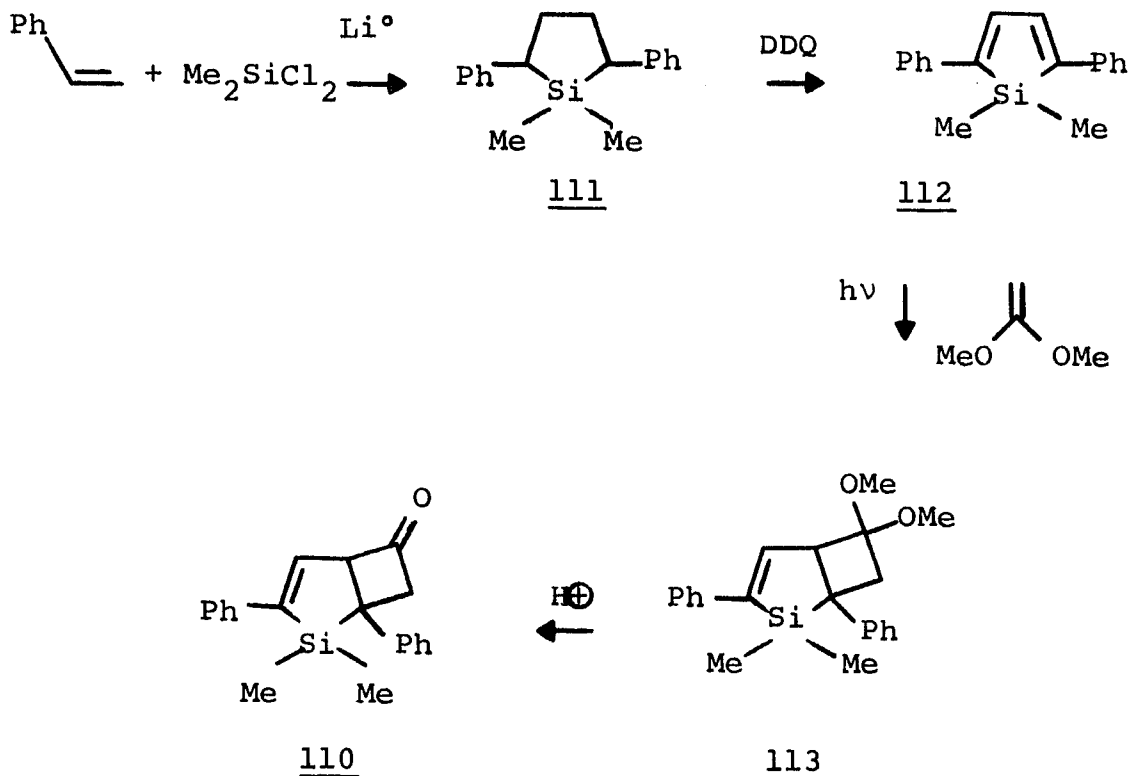
RESULTS AND DISCUSSION

The primary objective of this aspect of the research program was to synthesize and investigate the properties of a silepin, as discussed in the following section. A secondary and related goal in this investigation was to study rearrangements in a bicyclic organosilicon system in view of the limited information available in this area (87).

The previous exploratory work by Nelson (88) demonstrated that an organosilicon bicyclic system might be a route to silepin 88, although the silepin was not thoroughly purified or characterized. It was this work that formed the starting point in the present investigations.

The basic starting material for the entire program was 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-one (110), the preparation of which had been outlined previously (88). Cyclization of dimethyldichlorosilane with styrene and lithium afforded 1,1-dimethyl-2,5-diphenylsilacyclopentane (111) as a mixture of cis and trans isomers. Dehydrogenation of 111 with 2,3-dichloro-5,6-dicyanoquinone (DDQ) gave good yields of 1,1-dimethyl-2,5-diphenylsilacyclopenta-2,4-diene (112) using the method developed by Barton and Gottsman (89). A photocyclization of 112 and 1,1-dimethoxyethylene using 1,1-dimethoxyethylene as the solvent formed 1,1-dimethyl-2,7-diphenyl-5,5-

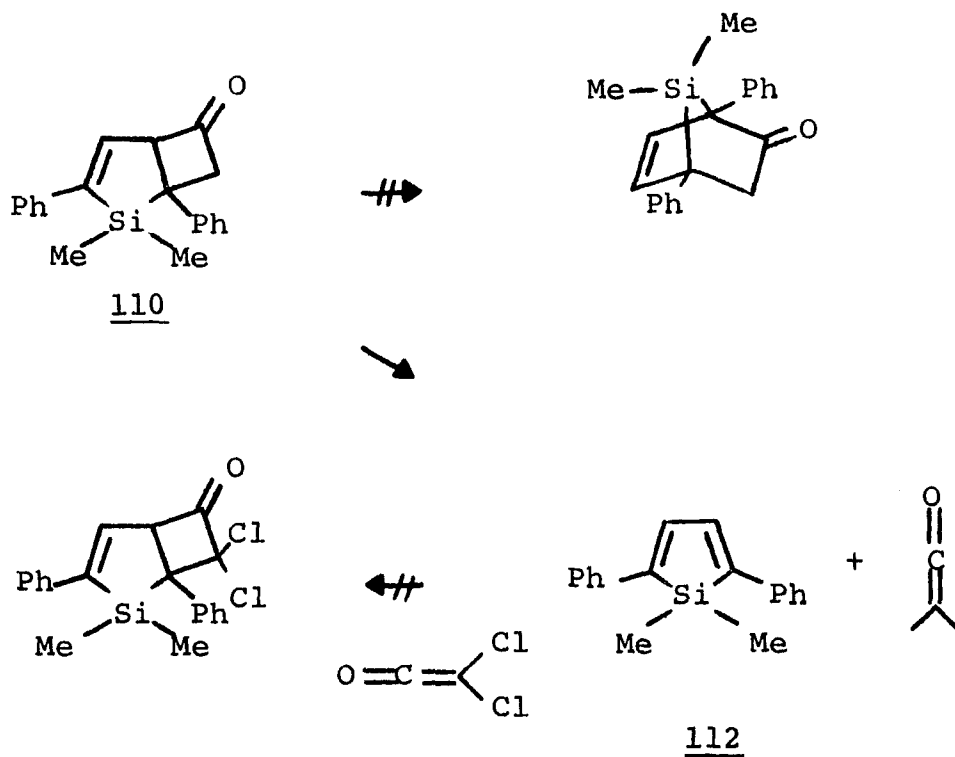
dimethoxy-1-silabicyclo[3.2.0]hept-2-ene (113) which was hydrolyzed to 110.



The diphenylbicyclo[3.2.0]ketone 110 was viewed as a good precursor to a silepin through the intermediacy of a 7-silanorbornene by direct analogy to the thermolysis of the carbon analog reported by Schiess and Funfschilling (86). Pyrolysis of the diphenylbicyclo[3.2.0] ketone 110 at 300° afforded only 1,1-dimethyl-2,5-diphenyl-1-silacyclopenta-2,4-diene (112) and (presumably) ketene. Although both the carbocyclic and organosilicon bicyclic systems react by a

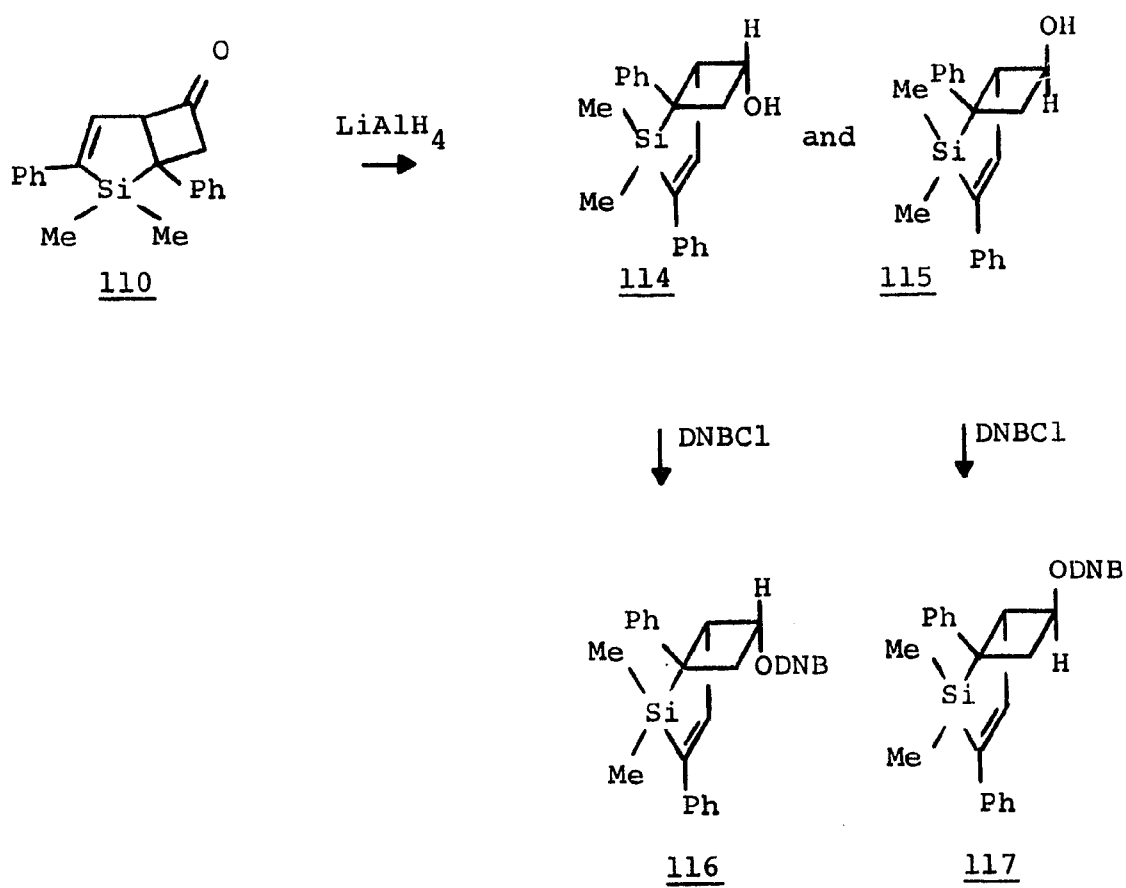
cycloreversion process, the reasons for the different direction of ring opening and the failure to form a sila-norbornene are not clearly understood.

These findings suggested that a more direct route to a bicyclo[3.2.0] system might be possible which would avoid the synthetically limiting photochemical reaction with 1,1-dimethoxyethylene. The more reactive ketene, dichloroketene, was generated at -20° , and silole 112 was added with warming to room temperature. No reaction was observed, and the starting silole was recovered almost quantitatively.



Our next approach to the problem was to investigate solvolytic reactions of bicyclic systems similar to those reported by Dryden (83) in carbocyclic systems. For this purpose a bicyclic[3.2.0] alcohol was a prerequisite for the necessary starting materials. Reduction of the diphenyl-bicyclo[3.2.0] ketone 110 with sodium borohydride in ethanol gave a 50:50 mixture of endo- and exo-1,1-dimethyl-2,5-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114) and (115) respectively in contrast to the stereoselective reductions observed in the carbon analogs (90). The endo alcohol 114 was isolated as a white crystalline solid after column chromatography while the exo isomer was obtained only as a viscous oil. The 3,5-dinitrobenzoate derivatives of both the endo- and exo-diphenyl alcohols 116 and 117 were obtained as crystalline solids and were fully characterized.

An important aspect of this problem is the complete structure assignment of the endo-alcohol 114, which was facilitated by spin-decoupling experiments, shown in Figures 1 and 2 and summarized in Table 2. H_C was assigned as the exo methylene proton because of the precedence of "W coupling" in cyclobutane rings where the interacting nuclei are in a cis arrangement (91). This is also consistent with the chemical shift of H_B relative to H_C . The endo methylene proton H_B is expected to lie in the shielding cone of the olefinic double bond and is therefore expected to be



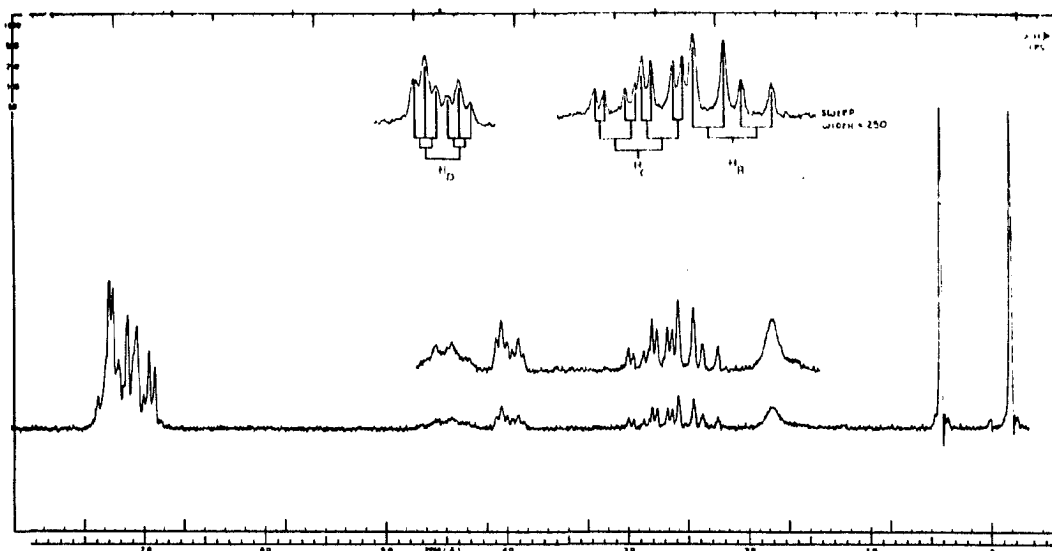


Figure 1. 60 MHz nmr spectrum of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114)

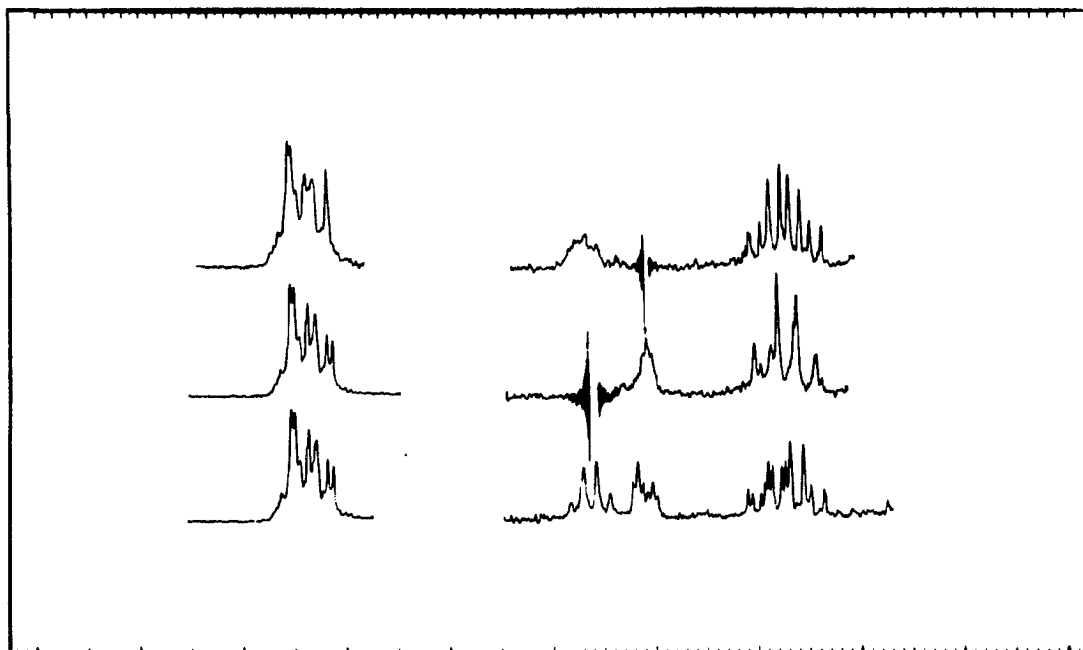
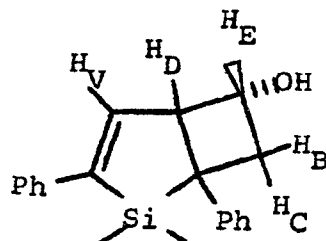


Figure 2. 60 MHz nmr spectrum of spin-decoupling of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114)

Table 2. Results of spin-decoupling experiments on endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114)



114

Irradiation Frequency	H_B δ 2.43	H_C δ 2.82	H_D δ 3.98	J_E δ 4.49	H_V δ 6.94
no irradiation	d of d $\underline{J}_{BC} = 12.0$ Hz $\underline{J}_{BE} = 7.5$ Hz	d of d of d $\underline{J}_{BC} = 12.0$ Hz $\underline{J}_{CD} = 2.5$ Hz $\underline{J}_{CE} = 7.5$ Hz	d of t	m	d $\underline{J}_{DV} = 3.0$ Hz
H_D 239 Hz	d of d $\underline{J}_{BC} = 12.0$ Hz $\underline{J}_{BE} = 7.5$ Hz	d of d $\underline{J}_{BC} = 12.0$ Hz $\underline{J}_{CE} = 7.5$ Hz			s
H_E 270 Hz	d $\underline{J}_{BC} = 12.0$ Hz	d of d $\underline{J}_{BC} = 12.0$ Hz $\underline{J}_{CD} = 2.5$ Hz			d $\underline{J}_{DV} = 3.0$ Hz

shielded and shifted upfield relative to the exo proton H_C . This was found to be the case in that H_B was 0.4 ppm upfield from H_C .

Absolute assignment of the stereochemistry of the two isomers was made by comparison of the nmr spectra of the endo- and exo-3,5-dinitrobenzoates 116 and 117 respectively, shown in Figures 4 and 3. The nmr spectrum of the endo-dinitrobenzoate 116 derived from the crystalline endo-alcohol 114 has two striking features in comparison with the exo-dinitrobenzoate 117 obtained from the exo-alcohol. The olefinic proton H_V of the endo-dinitrobenzoate 116 is shifted upfield from the aromatic protons by approximately 0.3 ppm in contrast to H_V of the exo-dinitrobenzoate 117 which is lost in the aromatic region. Inspection of the two isomers shows that the olefinic proton of the endo isomer is directed into the aromatic dinitrobenzoate shielding cone and therefore shifted upfield relative to the exo dinitrobenzoate. An ideal model compound for this analogy is exo-1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (118, page 102) in which the olefinic proton is also shielded, resulting in an upfield shift of 0.7 ppm.

The other noticeable feature of the nmr spectrum of the dinitrobenzoates is the hydroxy methine proton H_E of the exo-dinitrobenzoate 117 which is shifted approximately 0.6 ppm upfield relative to the endo-dinitrobenzoate 116. An examination

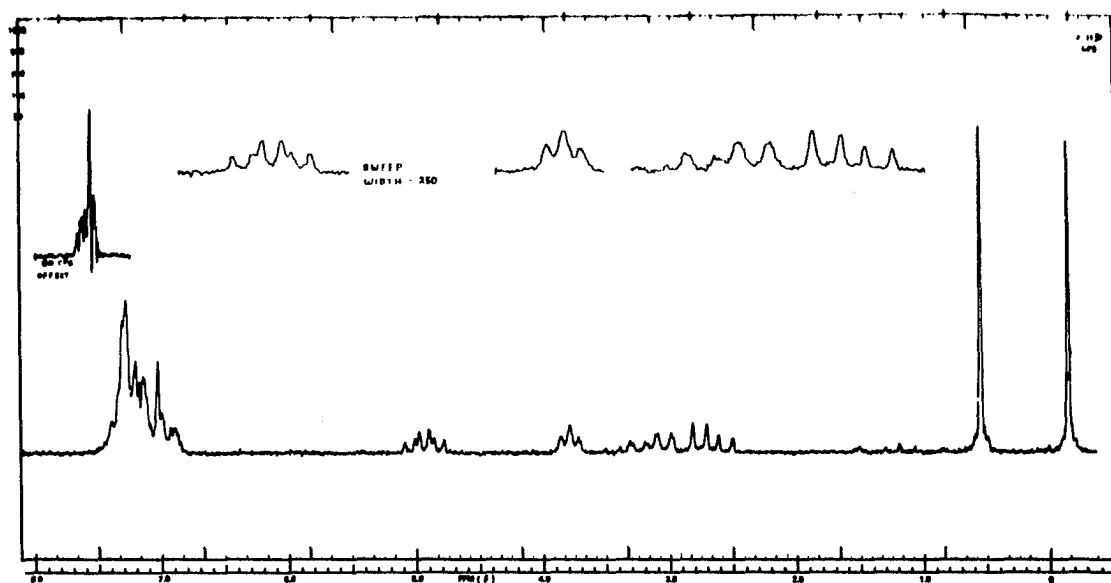


Figure 3. 60 MHz nmr spectrum of exo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl 3,5-dinitrobenzoate (117)

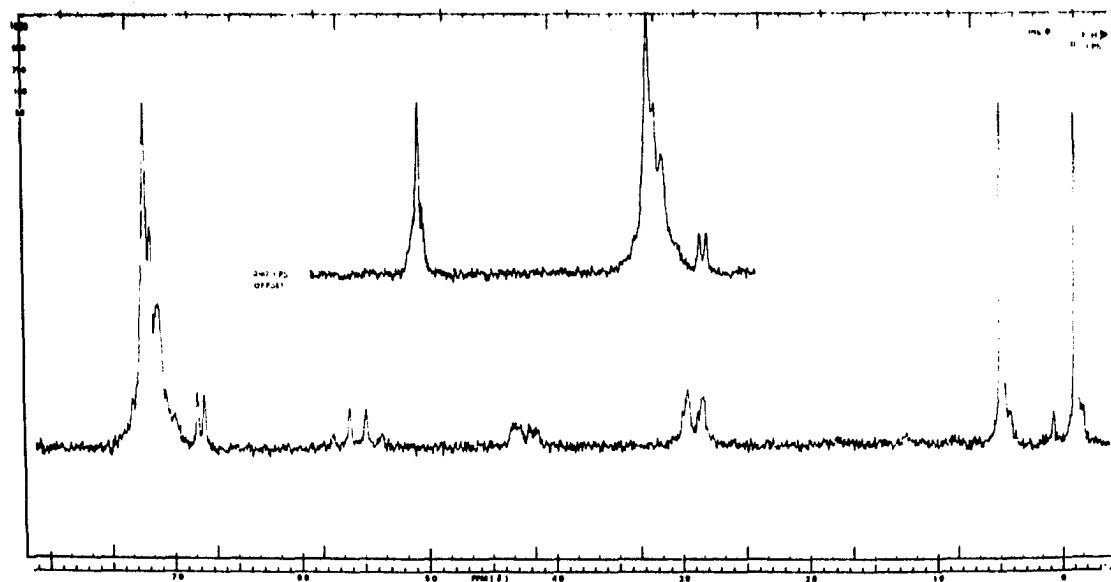
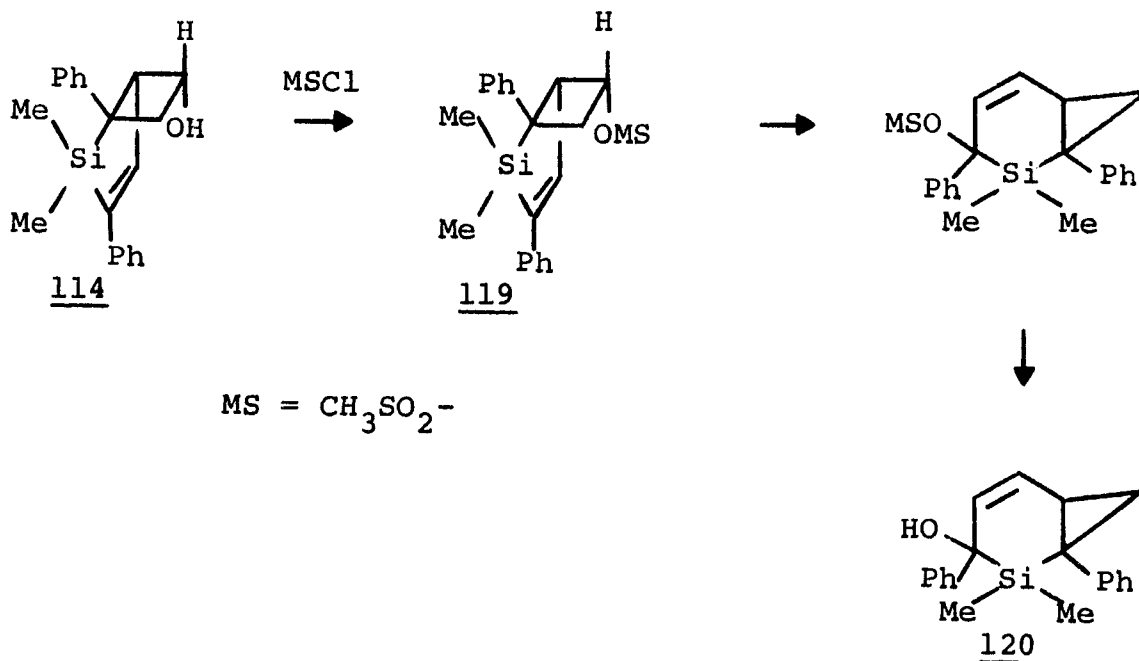


Figure 4. 60 MHz nmr spectrum of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl 3,5-dinitrobenzoate (116)

of models of the two systems again shows that the hydroxy methine proton H_E of the exo dinitrobenzoate is directly in the shielding cone of the double bond and expected to appear at higher fields than the hydroxy methine proton of the endo dinitrobenzoate which is oriented away from the olefinic shielding cone.

Solvolysis of the endo-dinitrobenzoate 116 as a route to silepin was prompted by the report that solvolysis of bicyclo [3.2.0]hept-2-ene-6-yl tosylate in buffered acetic acid afforded cycloheptatriene in a 50% yield (83). The endo-dinitrobenzoate 116 was heated under reflux for 6 days in 90% aqueous ethanol containing a urea buffer. The ester was very resistant to solvolysis, and some starting material was present even after 6 days. The two main products of the reaction were identified as ethyl-3,5-dinitrobenzoate and the endo-alcohol 114. No product could be found in which the cyclobutane carbon-oxygen bond was broken in preference to acyl cleavage. This resistance to solvolysis in ethanol--water led to a second solvolysis attempt in which trifluoroethanol was used as a solvent. Trifluoroethanol has been promoted recently as a superior solvent with good ionizing ability and very low nucleophilicity in solvolysis reactions (92). After refluxing the endo-dinitrobenzoate 116 in neat trifluoroethanol for 24 hours, the starting material was recovered unchanged.

Another solvolytic route to silepin was considered via 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl methane sulfonate (119). When the endo-alcohol 114 was treated with methanesulfonyl chloride, followed by quenching with water, a clear, impure oil was isolated by column chromatography on silica gel. Further purification could not be effected, and the product was found to be unstable on silica gel. On the basis of the nmr spectrum the structure was tentatively assigned as 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[4.1.0]hept-3-ene-2-ol (120). A comparison of the nmr spectra of the rearranged bicyclo[4.1.0] alcohol 120 and an immediate nmr spectrum of the reaction mixture revealed that the initially formed product (presumably 119) was unstable and underwent further reaction over a period of four hours.



The failure of these solvolysis experiments suggested that a silabicyclo[3.2.0] cation might be generated more directly from the endo-diphenyl alcohol 114. The classical dehydration method of the early German chemists was attempted with a catalytic amount of p-toluenesulfonic acid in refluxing benzene. A recirculating Dean-Stark trap filled with molecular sieves was employed in the reaction to ensure complete removal of small amounts of water. The reaction was followed by tlc for 24 hours until no further change could be detected. A careful investigation of the reaction showed the formation of numerous products which were identified and isolated by several methods. Column chromatography on silica gel, eluting with hexane, separated an oil which had three components. Crystallization from hexane gave m-terphenyl (121) in an overall yield of 24% as identified by nmr and melting point comparison with an authentic sample. Liquid-liquid chromatography of the residual oil showed 3% of o-terphenyl (122) as identified by liquid-liquid chromatography retention times. Liquid-liquid chromatography showed that no p-terphenyl was formed in this reaction, even in trace amounts. The second component in the hexane chromatographed oil was isolated and purified by liquid-liquid chromatography and identified as 1,1-dimethyl-2,7-diphenyl silepin (123), 11% (nmr yield). The silicon methyl protons of the silepin appear as a singlet in the nmr spectrum, Figure 5, at δ 0.10 which

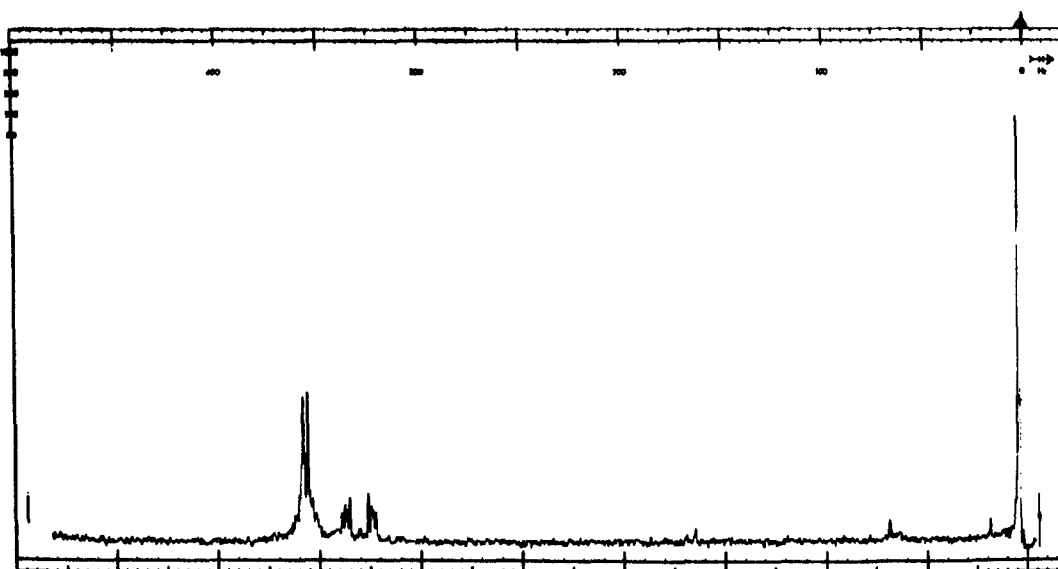


Figure 5. 100 MHz nmr spectrum of 1,1-dimethyl-2,7-diphenyl-silepin (123)

suggests either a rapidly inverting boat geometry, a planar geometry or a noninverting boat geometry with fortuitous nmr equivalence of silicon methyl groups. A good model compound for the silepin is 1,6,7-triphenyltropyliene, prepared by a previously reported method (93). The olefinic protons of 1,6,7-triphenyltropyliene appear as an AA'BB' eight-line spectrum on an 100 MHz scale-expanded spectrum (lower field protons further split) with centers at δ 6.40 and δ 6.71, $J_{\text{apparent}} = 3.0, 4.5$ Hz.

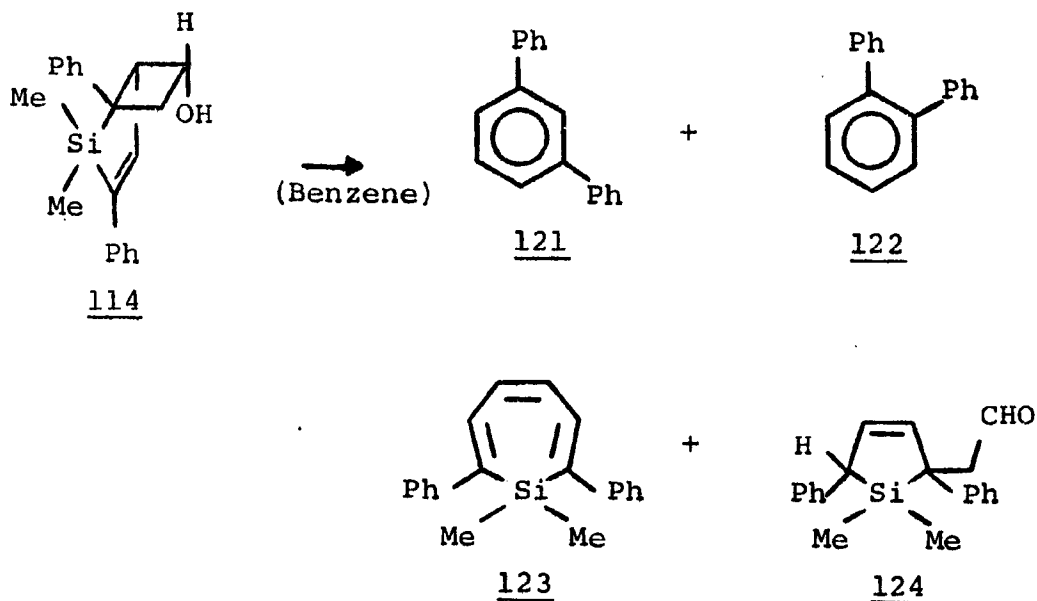
This can be compared with the olefinic protons of silepin

which also appear as an AA'BB' eight-line spectrum with centers at δ 6.51 and δ 6.80, $J_{\text{apparent}} = 3.0, 4.5$ Hz. The mass spectrum of 123 shows a strong parent ion at m/e 288 with methyl loss and dimethylsilylene loss as major fragmentations at 70 ev. At 24 ev the parent ion is the base peak.

Trapping experiments were attempted with a silepin-terphenyl mixture and various dienophiles. Maleic anhydride and the silepin did not react, even when heated to 130° for 12 hr. A more reactive dienophile, tetracyanoethylene, also did not react at 60°. Increased heating to 150° resulted in decomposition to a mixture of terphenyls.

Further elution with 50% ether--hexane removed the fourth component of the reaction which was identified by nmr comparison with an authentic sample as 1,1-dimethyl-cis-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (124), 12.2%. Small amounts of the starting alcohol 114 were also observed by nmr in the latter fractions of the 50% ether--hexane elution.

It should be noted that the aldehyde 124 is isomeric with the starting endo-diphenyl alcohol 114 and as such might be a thermal rearrangement product of the starting alcohol, because the reaction was carried out in refluxing benzene. If this were the correct mechanism, it would be expected that higher temperatures would result in higher yields of the aldehyde 124. This was very clearly shown when the endo-



diphenyl alcohol 114 was pyrolyzed at 300° in a vertical pyrolysis apparatus to afford 124, almost quantitatively, as shown by the nmr spectrum in Figures 6 and 7.

The structure of aldehyde 124 was assigned using the spin-decoupling experiment shown in Figure 8 and summarized in Table 3. An examination of stereochemical models of the endo-diphenyl alcohol 114 revealed that the hydroxyl proton is very proximate to the olefinic benzylic carbon and suggested the 6e⁻ concerted mechanism for the formation of 124 shown in Scheme 9. An alternate mechanism might involve a diradical process in which an initial homolytic cleavage of the cyclobutane carbon bond could be followed by hydrogen transfer and rearrangement to the same

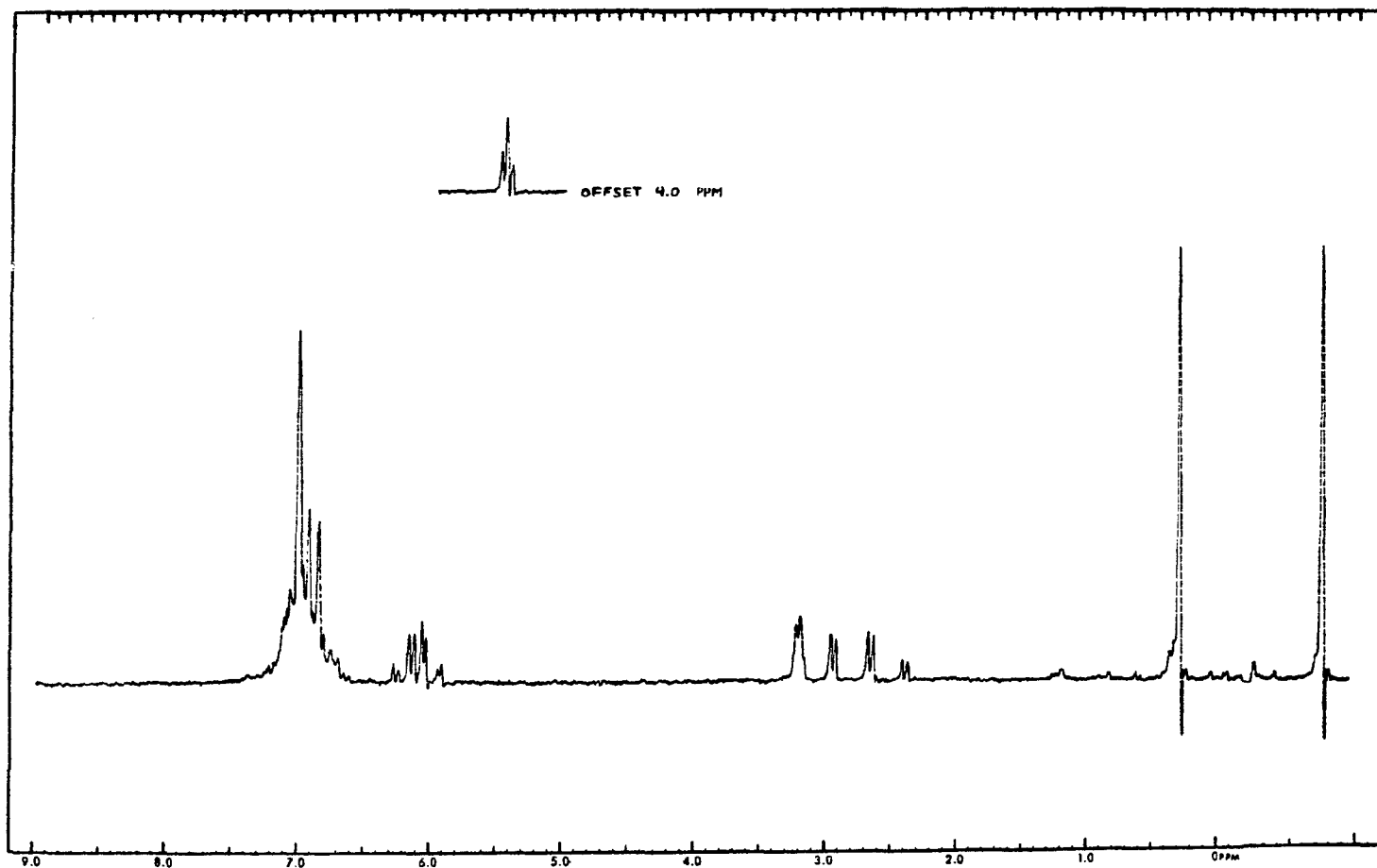


Figure 6. 60 MHz nmr spectrum of 1,1-dimethyl-cis-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (124)

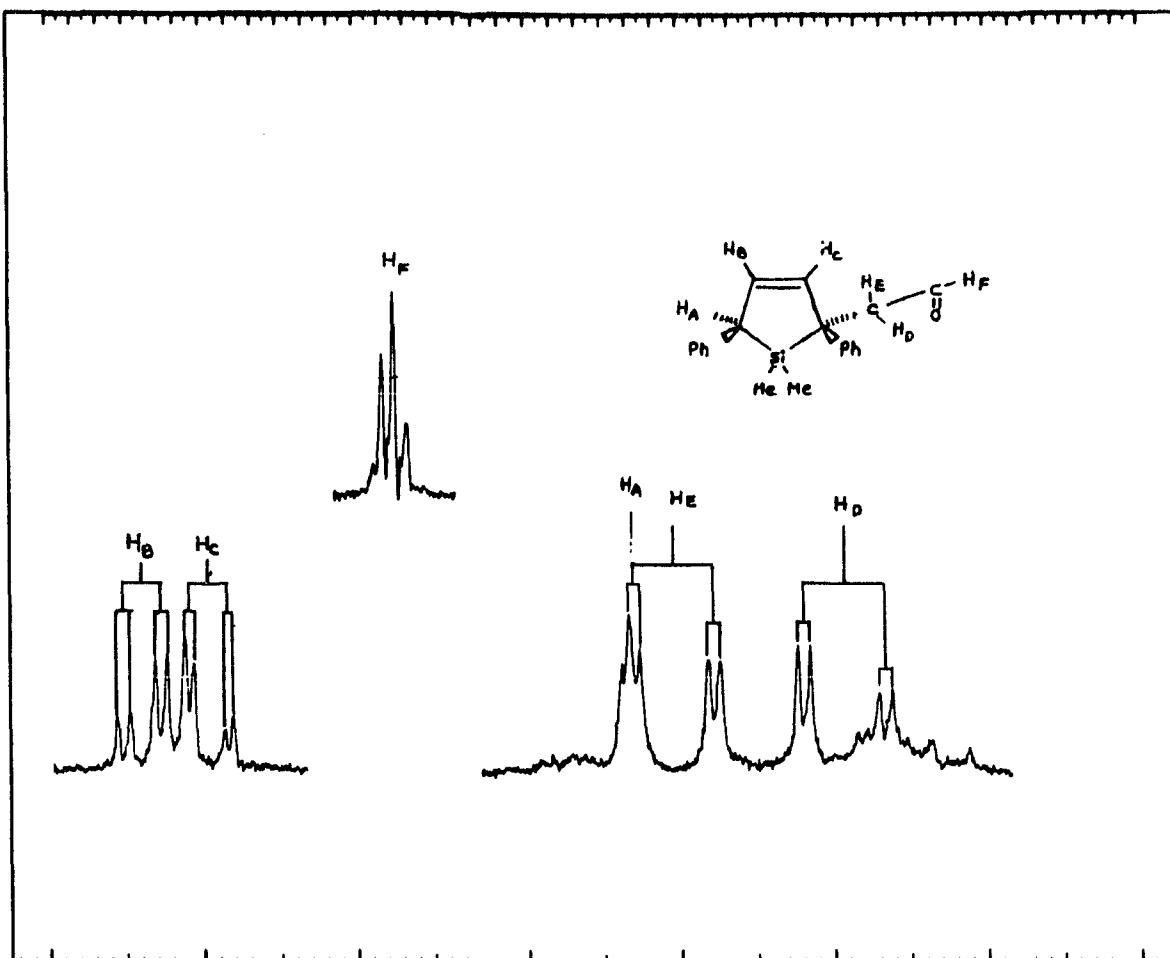


Figure 7. 60 MHz nmr spectrum of 1,1-dimethyl-cis-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (124)

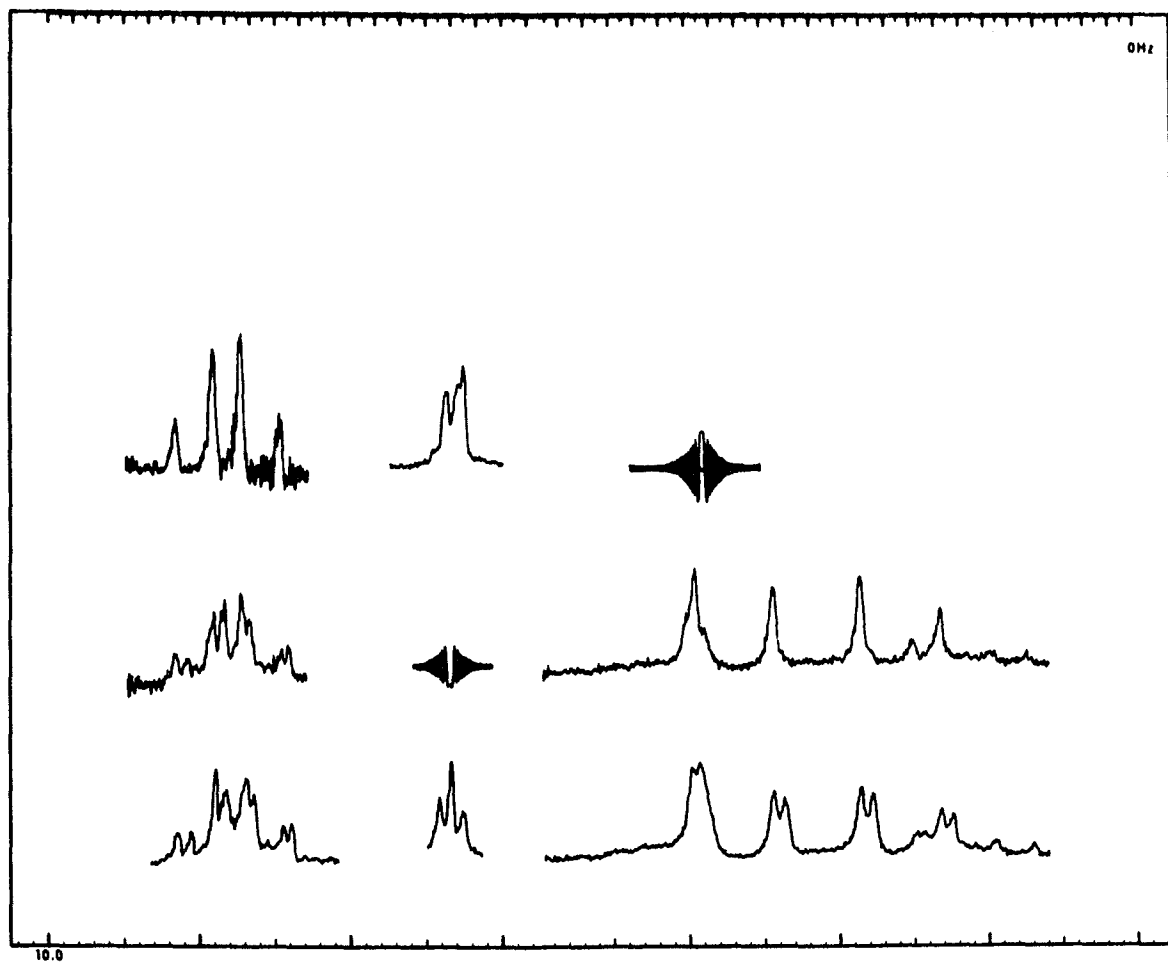
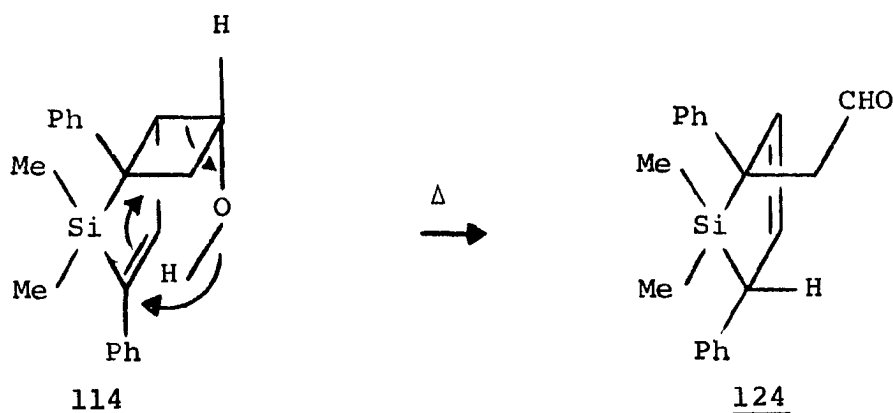


Figure 8. 60 MHz nmr spectrum of spin-decoupling of 1,1-dimethyl-cis-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (124)

Table 3. Results of spin-decoupling experiments on 1,1-dimethyl-cis-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (124)

Irradiation Frequency	H _A δ 2.43	H _B δ 6.00	H _C δ 6.21	H _D δ 2.51	H _E δ 3.04	H _F δ 9.44
no irradiation	?	d of d J _{BC} = 7.0 Hz J _{AB} = 3.0 Hz	d of d J _{BC} = 7.0 Hz J _{AC} = 2.0 Hz	d of d J _{DE} = 18.0 Hz J _{DF} = 3.0 Hz	d of d J _{DE} = 18.0 Hz J _{EF} = 2.0 Hz	t t
H _A 195 Hz		d J _{BC} = 7.0 Hz	d J _{BC} = 7.0 Hz			
H _F 566 Hz		d of d J _{BC} = 7.0 Hz J _{AB} = 3.0 Hz	d of d J _{BC} = 7.0 Hz J _{AC} = 2.0 Hz	d J _{DE} = 18.0 Hz	d J _{DE} = 18.0 Hz	

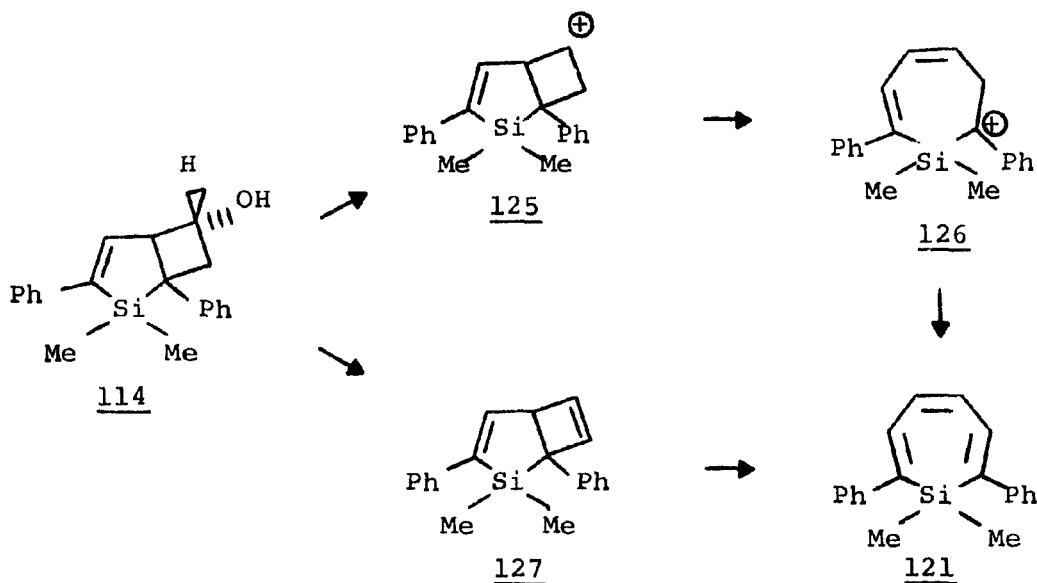
Scheme 9



product. Such a process is not expected to be stereoselective and therefore not consistent with the finding that only one isomer is formed. Pyrolysis of the exo alcohol would be expected to form the same aldehyde product if the diradical mechanism were operative. When the exo alcohol pyrolysis was carried out, none of the aldehyde 124 was formed, and only uncharacterized products were obtained. This result is consistent with the concerted mechanism. The stereochemistry is tentatively assigned as *cis* on the basis of the expected geometry of the concerted mechanism.

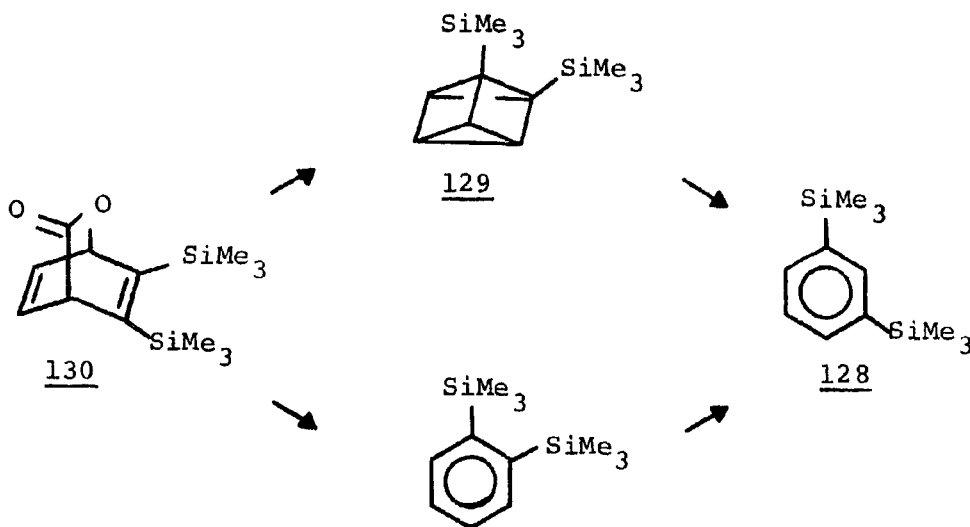
Two possible mechanisms can be envisioned for the formation of silepin. Protonation of the endo-diphenyl alcohol 114 and dehydration would give rise to the cyclobutyl cation 125, which could rearrange to the allylcarbinyll ion 126 and deprotonate to form 123. An alternate mechanism would be

the dehydration of 114 to afford 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hepta-2,5-diene (127), followed by cyclobutene ring opening to 121. It should be noted however that the latter pathway is not considered as likely because carbocyclic and heterocyclic bicyclo[3.2.0]heptadiene ring openings require higher temperatures (42, 81).



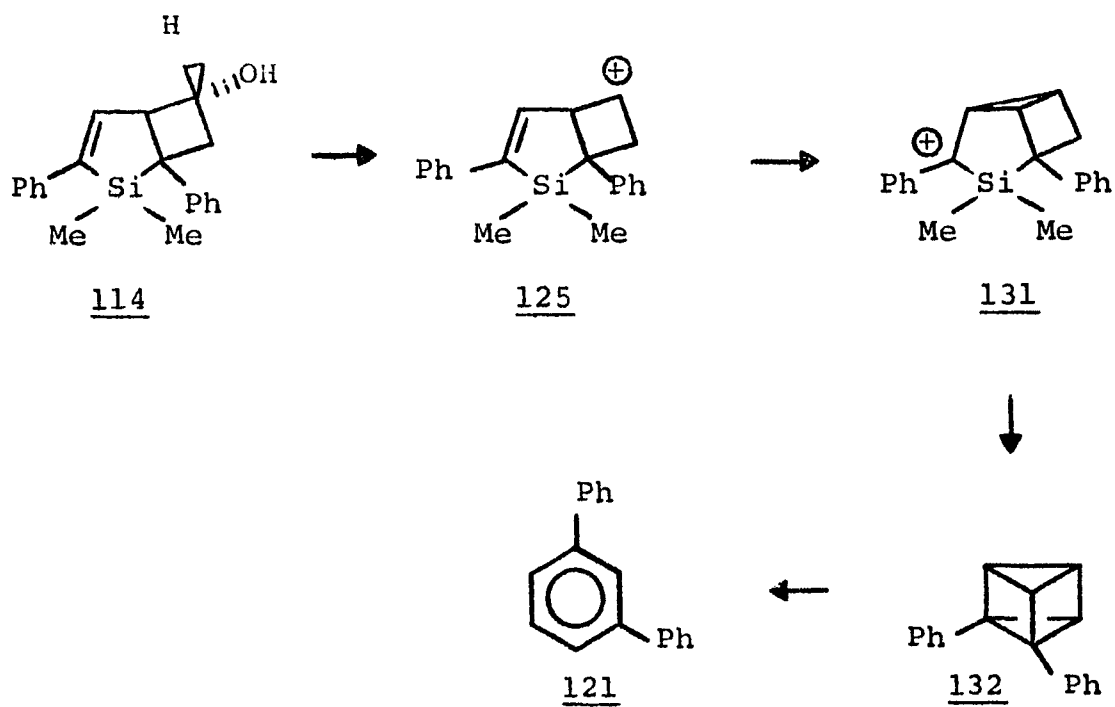
Although the finding of m-terphenyl in the reaction was surprising, a literature search revealed that similar isomerizations were not unprecedented. Seyferth et al. (94) found that a Diels-Alder reaction of α -pyrone and bis(trimethylsilyl)acetylene in bromobenzene at 140° afforded predominantly m-bis(trimethylsilyl)benzene (128) with only traces of the o- and p-isomers. It was proposed that a prismane

intermediate 129 was formed from the initial Diels-Alder adduct 130 by an unspecified mechanism. Cleavage of the cyclopropane ring between the two trimethylsilyl groups would form 128. A reinvestigation (95) of this reaction, however, revealed that 128 was formed by acid catalyzed isomerization of o-bis(trimethylsilyl)benzene in the presence of small amounts of acid in the reaction mixture.

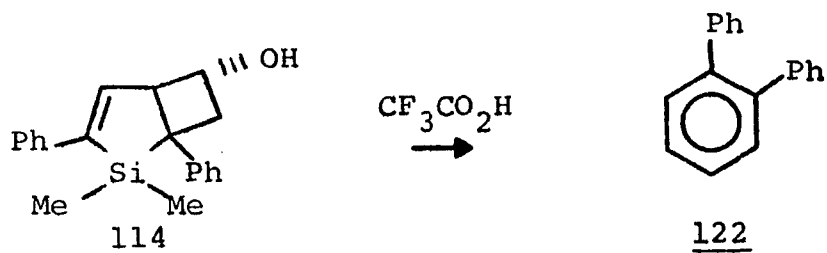


Prompted by the findings of Seyferth et al., the stabilities of o-, m- and p-terphenyl were investigated in the presence of p-toluenesulfonic acid in refluxing benzene. No product isomerizations were observed, and this mechanism was eliminated from consideration in favor of the following. The initial ion 125 formed by protonation and dehydration of the

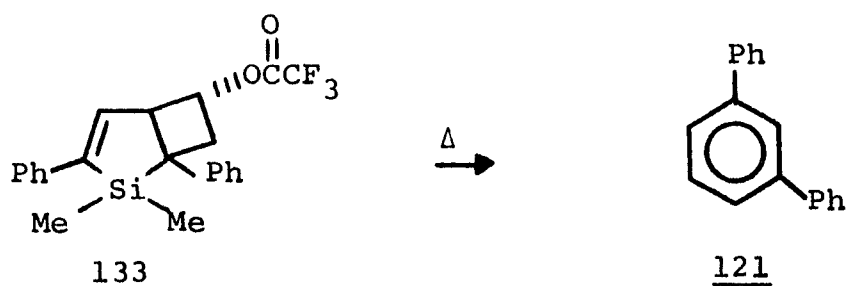
endo-diphenyl alcohol is a homoallylic ion and as such can isomerize to the cyclopropylcarbinyll ion 131 which is also a tertiary benzylic carbonium ion. This ion can deprotonate and lose silylene to form the diphenyl prismane 132 with both phenyls on the same cyclopropane ring. Although the conversion of prismane to benzene is not a symmetry allowed process according to Woodward and Hoffmann (79), cleavage is expected to occur predominantly between the two phenyls to form m-terphenyl by formation of the most stable diradical. It should be noted that the prismane is never demanded as an intermediate in the mechanism. Burgstahler and Chien (96) have also proposed a prismane intermediate in a photo-isomerization of o-di-*t*-butylbenzene to a mixture of meta and para isomers.



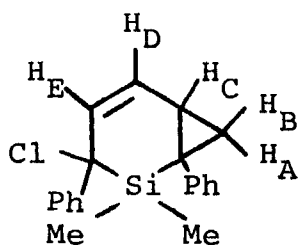
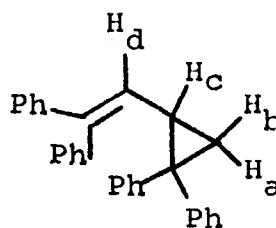
It seemed that it might be possible to reduce the thermal rearrangement to m-terphenyl, and therefore increase the amount of silepin by carrying out the reaction at a lower temperature. The endo-diphenyl alcohol 114 was therefore treated with trifluoroacetic acid at room temperature. Although the amount of m-terphenyl was reduced to zero by this process, only a 35% yield of o-terphenyl and no silepin was isolated. Presumably, the silepin could be formed and rearrange to o-terphenyl via a silanorcaradiene under the reaction conditions.



In order to consider the mechanism for silepin formation via a diene intermediate it was desired to prepare 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hepta-2,5-diene (127). For this purpose the precursor endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl trifluoroacetate (133) was prepared from the corresponding alcohol. Pyrolysis of 133 at 250° did not form the desired diene 127 but rather a 19.9% yield of m-terphenyl.

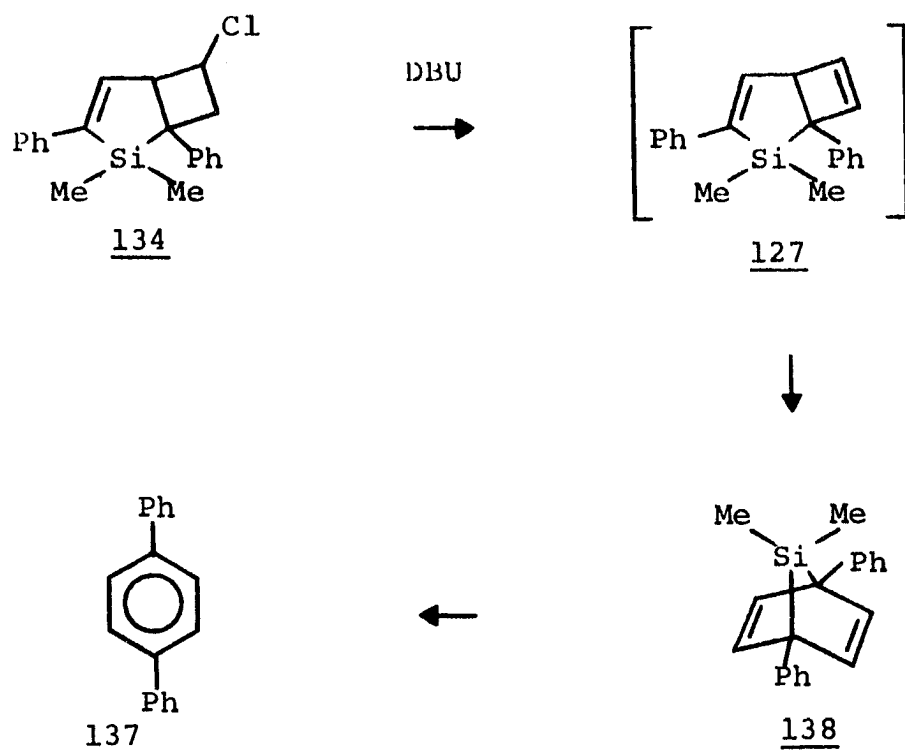


Another route to the diene intermediate 127 was sought that could be carried out at lower temperatures and possibly avoid the m-terphenyl formation. When the endo-alcohol 114 was treated with thionyl chloride in pyridine, a mixture of chlorides was obtained as determined by nmr spectroscopy. The major product was isolated and identified as 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl chloride (134) in which the stereochemistry was assumed to be exo from the well established stereochemical route of this conversion in pyridine. Another product in the reaction mixture was 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[4.1.0]hept-3-ene-2-yl chloride (135), presumably formed by a cyclobutyl cyclopropylcarbinyl rearrangement. These products are unstable to silica gel chromatography, but the nmr evidence is unambiguous. The rearranged isomer 135 showed a multiplet at δ 1.10 in the nmr spectrum for the geminal cyclopropyl protons H_A and H_B which can be compared to δ 1.50-1.54 for the geminal cyclopropyl protons H_a and H_b in the model compound 136. The cyclopropylallyl proton H_C , at δ 1.90 can be compared with H_c at δ 2.36 in the model compound 136 (97).

135136

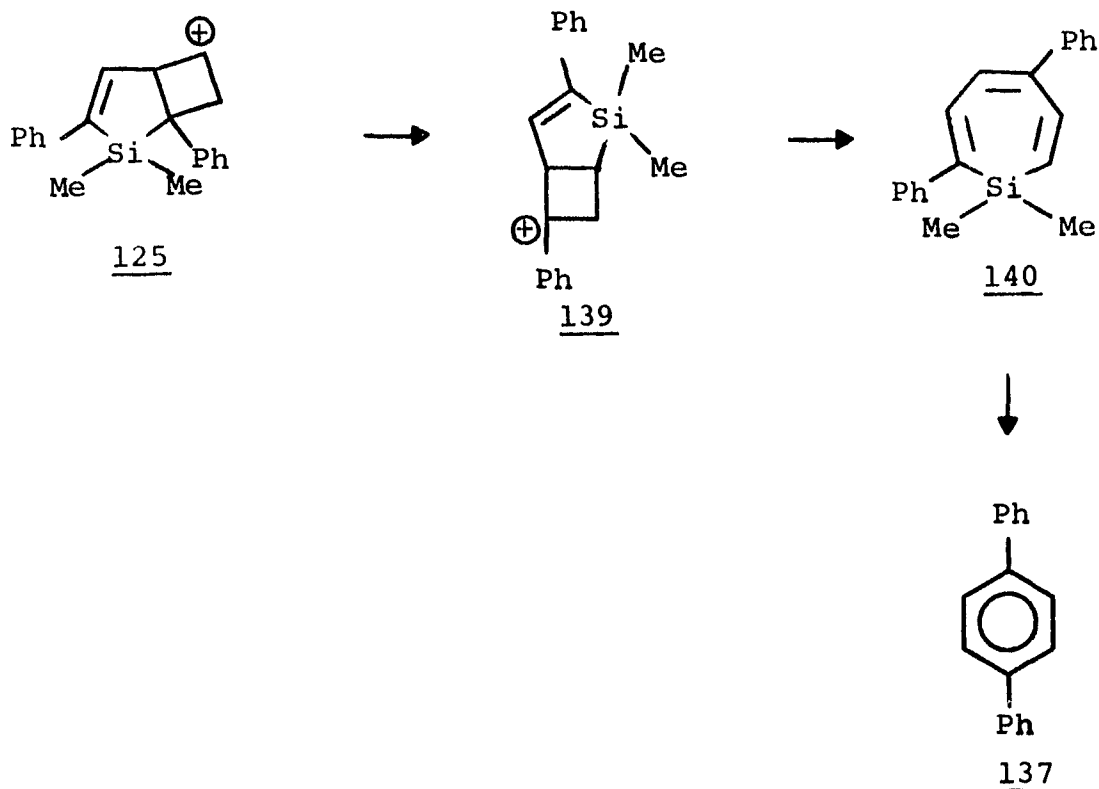
A solution of 134 and 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in acetonitrile did not undergo reaction at room temperature but required heating to 60°. The desired dehydrohalogenation product 127 was not obtained but instead a small amount of *p*-terphenyl was isolated. A mechanism for the formation of *p*-terphenyl (137) which can be written for this reaction is one in which dehydrohalogenation formed 127 followed by a 1,3-sigmatropic rearrangement with inversion to form 2,5-diphenyl-7,7-dimethyl-7-silanorbornadiene (138). The precedented elimination of silylene from silanorbornadiene systems (78) would then explain the formation of *p*-terphenyl.

A different 1,3 rearrangement of the diphenyl[3.2.0] system can be visualized in which a carbon-silicon bond is broken and migrated to a cationic center to form the tertiary benzylic carbonium ion 139. Proton loss and rearrangement would lead to 1,1-dimethyl-2,5-diphenylsilepin (140). By



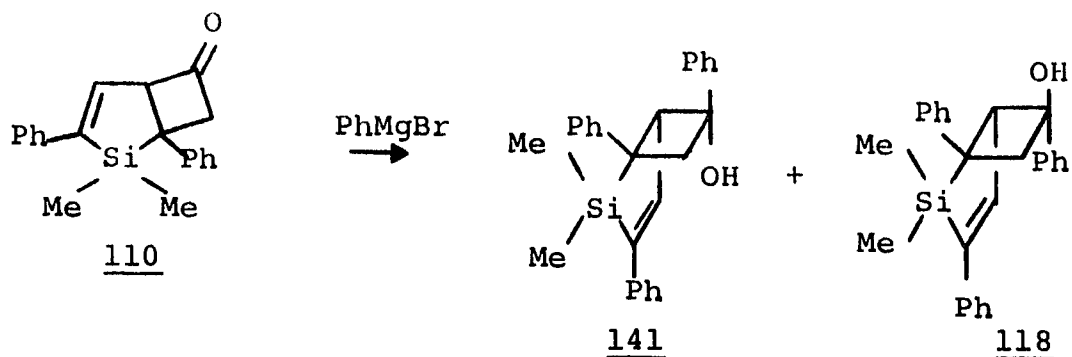
analogy to the carbocyclic diphenyl cycloheptatriene 102, an isomerization of 140 to the silanorcaradiene followed by silylene loss could form *p*-terphenyl (137). This mechanism would explain *p*-terphenyl formation, but a study (98) of 1,3 substituted cyclobutanes showed no enhancement in solvolysis reactions and argued against 1,3 rearrangements. At present there is no means of distinguishing between a mechanism involving the silanorbornadiene 138 and the diphenylsilepin 140.

The failure to synthesize 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hepta-2,5-diene and the competing rearrangements prompted the preparation of a system in which



the 5 position of the bicyclo[3.2.0] skeleton would be substituted with an aromatic substituent to stabilize the resulting carbonium ion. Phenyl magnesium bromide was added to 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-one to form a 50:50 mixture of endo- and exo-1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (141) and (118) respectively. The isomers were separated by chromatography and fractional crystallization, and the structures of the separated isomers were established with the aid of spin-

decoupling experiments, shown in Figure 11 and summarized in Table 4.



The nmr spectrum of the endo-alcohol **137**, shown in Figure 10, was fortuitously simple. The olefinic proton was covered by the aromatic multiplet. The corresponding olefinic proton of the exo-alcohol **118** was directly in the shielding cone of the endo phenyl group and was accordingly shifted upfield to δ 6.15.

The direct *p*-toluenesulfonic acid catalysis method was again employed in the dehydration of the triphenyl alcohol **118**. It was expected that the initially formed cyclobutyl cation **142**, as a tertiary benzylic carbonium ion, might be of greater or comparable stability compared to the strained cyclopropylcarbinyl ion **143** and as such proceed via path b instead of path a, shown in Scheme 10. It should be noted that the additional phenyl substituent provided a new label to distinguish between path a and path b, because the final products of these two pathways are 1,2,4-triphenylbenzene

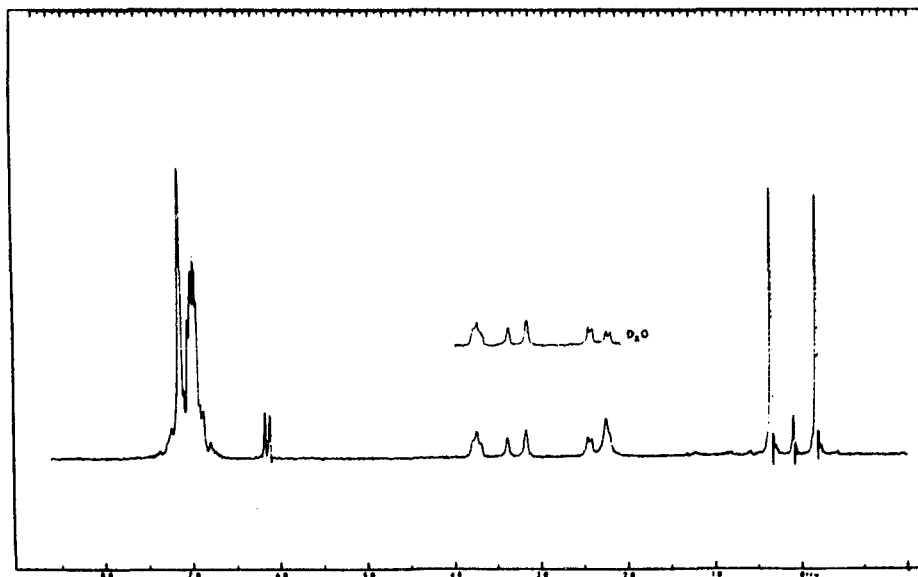


Figure 9. 60 MHz nmr spectrum of exo-1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (118)

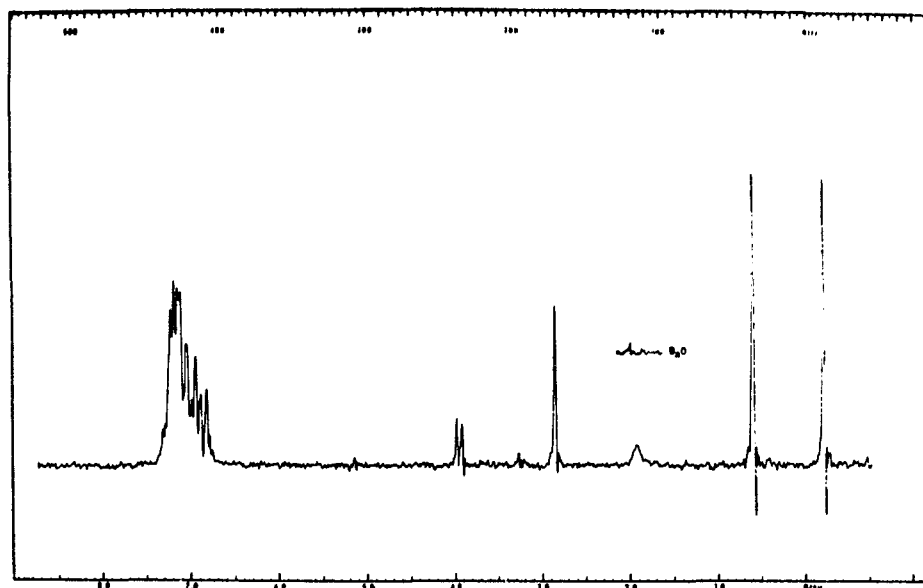


Figure 10. 60 MHz nmr spectrum of endo-1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (141)

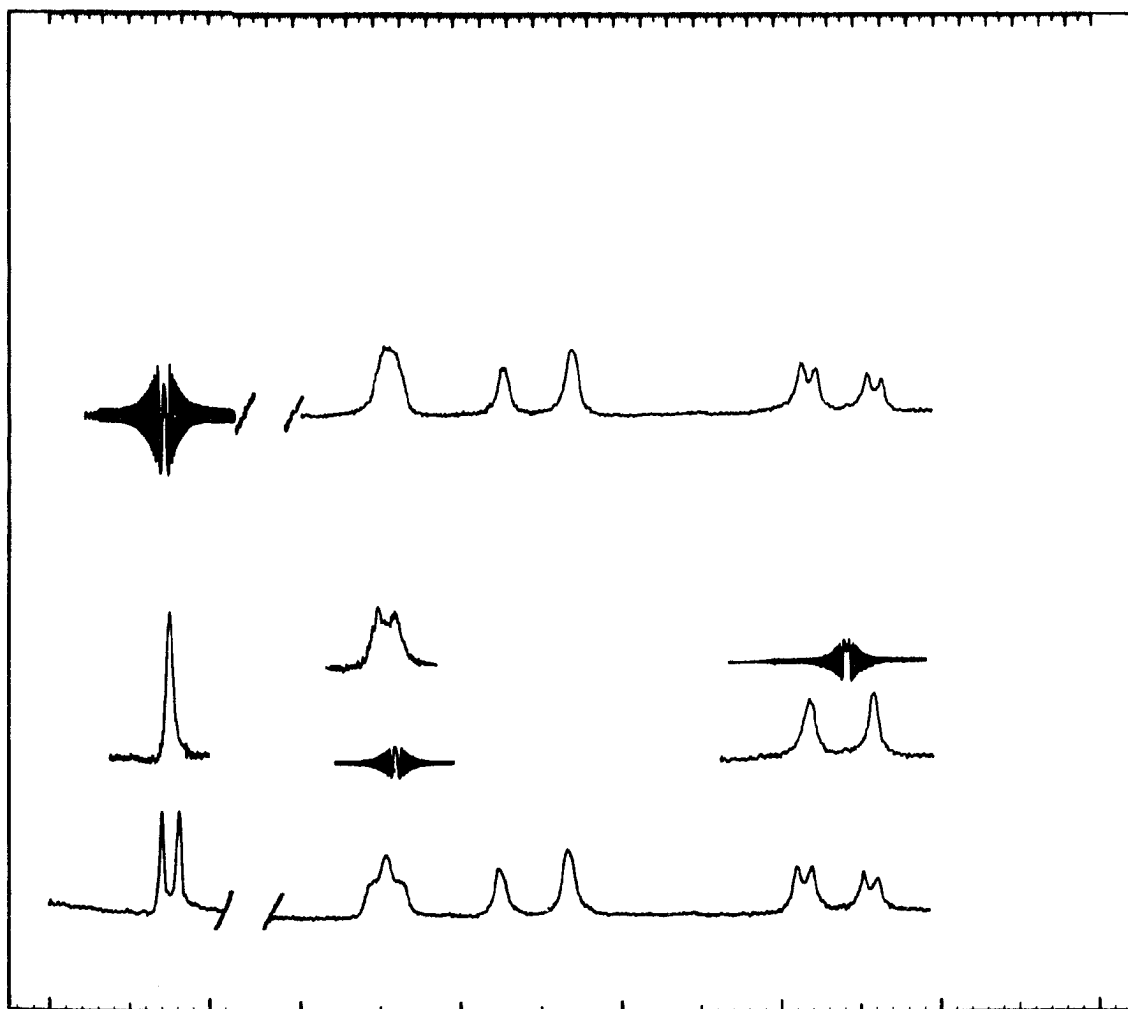


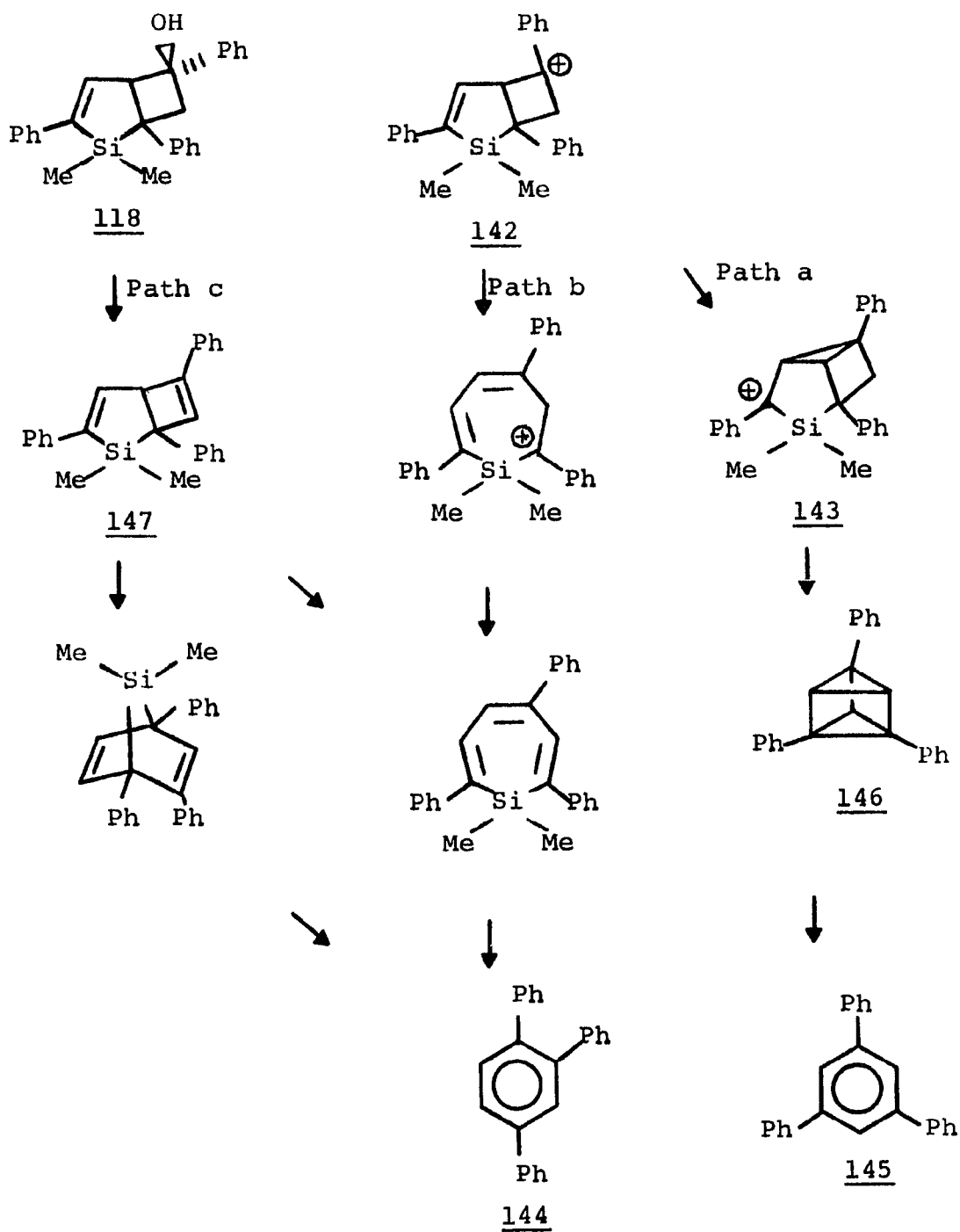
Figure 11. 60 MHz nmr spectrum of spin-decoupling of exo-1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (118)

(144) and 1,3,5-triphenylbenzene (145) respectively. After heating the triphenyl alcohol 118 for 12 hr in refluxing benzene with *p*-toluenesulfonic acid, a 57% yield of 1,2,4-triphenylbenzene was obtained and argued against path a involving the prismane intermediate 146 for this particular alcohol.

To distinguish between an ionic mechanism such as path b and a mechanism involving 1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hepta-2,5-diene (147), by path c, the triphenyldiene was synthesized by chlorination of the alcohol 118 followed by elimination with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU). A good model compound for nmr comparison with triphenyl diene 147 is 1,2,2-trimethyl-3-phenylbicyclo[3.2.0]hepta-3,6-diene (104). In both compounds the highest upfield olefinic proton is the cyclobutenyl proton at δ 5.80 in 104 and at δ 6.70 in 147. The bridgehead proton was reported at δ 3.20 in the nmr spectrum of 104 while the bridgehead proton of 147 is δ 4.15. The downfield shifts of the bridgehead and olefinic protons of 147 are consistent with the effects of the additional two β phenyl substituents.

After heating the triphenyl diene 147 in refluxing benzene for 18 hr, the starting material was recovered unchanged, and thereby eliminated path c from consideration. However the possibility remains that the triphenyl diene 147 is a

Scheme 10



transient intermediate that is rapidly protonated to an ion such as 142 under the reaction conditions.

EXPERIMENTAL

Infrared spectra (ir) were recorded on a Beckman 12 spectrophotometer. Routine nmr spectra were determined on a Varian model A-60 or a Hitachi R20-B spectrometer, and chemical shifts were reported as parts per million (δ scale) from tetramethyl silane as an internal standard. Decoupling and low temperature studies were recorded on the Hitachi R20-B spectrometer. The Varian HA-100 spectrometer was used to record all 100 MHz spectra. Routine mass spectra were obtained on an Atlas CH-4 spectrometer. High resolution mass spectra were recorded on a MS-902 mass spectrometer manufactured by AEI. Ultraviolet spectra (uv) were recorded using a Cary model 14 spectrophotometer. All melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Ilse Beetz Mikronanalytisches Laboratorium, Kronach, West Germany.

1,1-Dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-one (110):

The procedure of Nelson (88) was used to prepare this compound as a yellow oil. Crystallization from hexane or methanol gave white shiny crystals, mp 72-73°.

Anal. Calcd for $C_{20}H_{20}OSi$: C, 78.90; H, 6.62. Found: C, 79.03; H, 6.49.

endo- and exo-1,1-Dimethyl-2,7-diphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-ol (114) and (115):

To a solution of 13.02 g (42.8 mmol) of silabicyclo-[3.2.0] ketone 110 in 600 ml of absolute ethanol was added 0.548 g (14.5 mmol) of sodium borohydride in 200 ml of absolute ethanol. After 50 min ethanol was removed by rotary evaporation, and the yellow oil was purified by chromatography on a 6 x 37 cm column of silica gel. Silole dimer and other impurities were removed by eluting with 5% ether--hexane. The mixture of endo- and exo-alcohols was removed from the column with 50% ether--hexane, collecting 50 ml aliquots. Fractions 52-74 containing both alcohols were combined and concentrated to a clear oil. Multiple crystallization and recrystallization from hexane allowed isolation of 2.10 g (16.2%) of the pure endo-isomer 114 as a white solid: mp 115-116°; nmr (CDCl₃) δ -0.17 (s, 3H), 0.42 (s, 3H), 1.82 (b, 1H, exchanges with D₂O), 2.43 center (d of d, 1H, $J_{BE} = 7.5$ Hz, $J_{BC} = 12.0$ Hz), 2.82 center (d of d of d, 1H, $J_{BC} = 12.0$ Hz, $J_{CD} = 2.5$ Hz), 3.98 center (apparent d of t, 1H, bridgehead, $J_{DV} = 3$ Hz, $J_{DE} = 8.5$ Hz), 4.49 (b, 1H, hydroxy methine), 6.94 (d, 1H, vinyl), 6.98-7.50 (m, 10H), (couplings were assigned using spin decoupling experiments, Figure 2); ir (KBr) 3300, 3090, 3065, 3040, 2980, 2910, 1980, 1580, 1500, 1255, 1100 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 307 (1), 306 (6) M⁺, 262 (100).

Anal. Calcd for $C_{20}H_{22}OSi$: C, 78.38; H, 7.23; Found: C, 78.37; H, 7.37.

The residual filtrates contained the exo-alcohol 115 which was isolated as an oil and could not be further purified by column chromatography, although a crystalline derivative 117 was prepared and characterized in the following experimental. Integration of the silicon methyl peaks in the crude reaction by nmr shows that the endo- 114 and exo- 115 alcohols are formed in a 1:1 ratio and thereby places the yield of exo alcohol at 16.2% based on the isolated pure endo alcohol.

endo-1,1-Dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl 3,5-dinitrobenzoate (116):

A solution of 0.140 g (0.46 mmol) of the endo-alcohol 114 in 5 ml of dry pyridine was treated with 0.115 g (0.50 mmol) of freshly recrystallized 3,5-dinitrobenzoyl chloride with ice bath cooling, stirred for one hour at 0° and placed in the freezer overnight. The solution was poured over 10 g of ice and extracted with 50 ml of methylene chloride. After drying over anhydrous magnesium sulfate, the methylene chloride solution was rotary evaporated to a white solid which was recrystallized from methylene chloride--hexane to obtain 0.152 g (66.3%) of crystalline endo dinitrobenzoate 116. An analytical sample was prepared by chromatography on silica gel: mp 162-164°; nmr ($CDCl_3$) δ -0.11 (s, 3H), 0.45 (s, 3H), 2.92

(m, 2H), 4.25 (m, 1H), 5.57 (d of d, 1H), 6.80 (d of d, 1H, vinyl), 6.90-7.37 (m, 10H), 9.07 (s, 3H); ir (KBr) 1740, 1600, 1550, 1500, 1350, 1280, 1170 and 1075 cm^{-1} ; mass spectrum (70 eV) m/e (rel intensity) 500 (< 1), 262 (100).

Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_6\text{Si}$: C, 64.78; H, 4.83; N, 5.60. Found: C, 64.71; H, 4.79; N, 5.49.

exo-1,1-Dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl 3,5-dinitrobenzoate (117):

The procedure followed was identical to that described above for the preparation of the endo dinitrobenzoate. A small amount of dinitrobenzoic acid was removed by chromatography on silica gel. Recrystallization of the product from methylene chloride--ether afforded 20.3% of large white prisms of 117: mp 165-166°; nmr (CDCl_3) δ -0.16 (s, 3H), 0.53 (s, 3H), 2.67 (d of d, 1H), 3.16 (d of d, 1H), 3.80 (apparent triplet, 1H, bridgehead), 4.98 (apparent triplet of doublets, 1H), 6.80-7.50 (m, 11H), 9.08 (m, 3H); ir (KBr) 1738, 1550, 1347, 1270 and 1160 cm^{-1} ; mass spectrum (70 eV) m/e (rel intensity) 500 (< 1), 262 (100).

Anal. Calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_6\text{Si}$: C, 64.78; H, 4.83; N, 5.60. Found: C, 64.85; H, 4.98; N, 5.55.

Pyrolysis of 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-one (110):

A solution of 0.100 g of the title compound in 4.0 ml of benzene was added dropwise over a period of 5 min into

a 1/2 in. x 12 in. pyrolysis tube, packed with Vycor chips, at 300° under nitrogen. Collection of the yellow oil at Dry Ice--isopropanol temperature afforded 0.079 g (79% recovery) of a yellow liquid.

Chromatography on 10 ml of silica gel, eluting with hexane, gave 0.041 g (36.1%) of 1,1-dimethyl-2,5-diphenyl-1-silacyclopenta-2,4-diene (112): mp 126-128° [lit. (99) 131-133°]; nmr (CDCl₃) δ 0.05 (s, 6H), 7.10-7.30 (m, 12H).

Attempted cyclization of 1,1-dimethyl-2,5-diphenyl-1-silacyclopenta-2,4-diene (112) and dichloroketene:

A solution of 0.262 g (1.00 mmol) of silole 112 and 0.111 g (1.10 mmol) of triethylamine in 50 ml of ether were cooled to -40°. A solution of 0.147 g (1.00 mmol) of dichloroacetyl chloride in 2 ml of ether was added dropwise under nitrogen, and the reaction was allowed to warm to room temperature. Triethylamine hydrochloride was removed by filtration, and the residual solution was concentrated to dryness. Recrystallization from methylene chloride--hexane afforded 0.20 g (76.2%) of starting silole 112 as yellow crystals, mp 131-133° [lit. (99) mp 131-133°]. The nmr spectrum of the crude reaction showed that silole was the only proton containing species present: nmr (CDCl₃) δ 0.55 (s, 6H), 7.2 (m, 12H).

Solvolysis of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl 3,5-dinitrobenzoate (116) in aqueous ethanol:

A solution of 0.073 g (0.145 mmol) of the title compound in 200 ml of 90% aqueous ethanol and 100 mg of urea buffer was heated under reflux for 6 days. Ethanol was removed by rotary evaporation; the residue was dissolved in 50 ml of methylene chloride, and washed with 20 ml of water. The methylene chloride layer was dried over anhydrous magnesium sulfate and concentrated to 0.043 g of dark oil. The residue was applied to a 20 x 20 x 0.1 cm preparative silica gel plate and eluted with 50% ether--hexane to afford two major components.

The first component, $R_f = 0.24$, was identified as ethyl 3,5-dinitrobenzoate, 0.011 g (31.5%). Recrystallization from ethanol gave crystals: mp 90-91° [lit. (100) mp 92°]; nmr (CDCl_3) δ 1.43 (t, 3H), 4.45 (q, 2H), 7.19 (s, 10H), 9.09 (s, 3H); ir (KBr) 3100, 1735, 1630, 1530, 1350, 1285 cm^{-1} .

The second component, $R_f = 0.14$, was identified as endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114), 0.010 g (13.7%), mp 113-114° (previous mp 115-116° of 114 obtained by reduction of ketone 110).

A small amount of residual starting material was also present by tlc comparison with authentic samples.

Attempted solvolysis of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl 3,5-dinitrobenzoate (116) in trifluoroethanol:

A solution of 0.082 g of the title compound in 10 ml of distilled trifluoroethanol was heated under reflux for 24 hr. Removal of the solvent by rotary evaporation afforded the starting dinitrobenzoate unchanged, mp 168-170°.

Attempted preparation of 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl methane sulfonate (119):

To a solution of 0.280 g (0.92 mmol) of alcohol 114 at 0° in 5 ml of pyridine was added 0.193 g (1.69 mmol) of methanesulfonyl chloride in 2.5 ml of dry pyridine. After 12 hr at freezer temperature the reaction was poured into 10 ml of water and 5 g of ice. The organic products were extracted with two 25 ml portions of ethyl ether and then washed with 25 ml of 1 N hydrochloric acid. After drying over anhydrous magnesium sulfate, the solvent was removed by rotary evaporation, and the residual oil was purified by column chromatography on silica gel. The major product was removed from the column with 50:50 ether--hexane to afford 0.102 g of colorless oil. The product was impure and repetitive chromatography revealed decomposition on silica gel. Some spectral data were obtained, however, and the rearranged structure, 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[4.1.0]hept-3-ene-2-ol (120), was tentatively proposed: nmr (CDCl₃) δ 0.10 (s, 3H), 0.23 (s, 3H), 1.10 (m, 2H), 1.80

(m, 2H, 1H exchanges with D_2O), 4.77 (d of d, 1H, $J = 3,6$ Hz), 6.55 (d of d, 1H, $J = 1,6$ Hz), (irradiation at δ 6.55 collapsed the absorption pattern at δ 4.77 to a simple doublet); ir (film) 3350 (broad) cm^{-1} ; mass spectrum (70 eV) m/e 306.

The same reaction was studied by nmr. As soon as the reaction was quenched and allowed to warm above 0° in the nmr probe, a rearrangement of an initially formed product (presumably a bicyclo[3.2.0]mesylate 119) was observed in which signals of 120 increased over a period of 4 hr.

Pyrolysis of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-ol (114):

A solution of 0.313 g (1.02 mmol) of the title compound in 2 ml of benzene was added dropwise over a period of 5 min into a 1/2 in. by 12 in. pyrolysis tube, packed with Vycor chips, at 300° under nitrogen. Collection of the yellow oil at Dry Ice--isopropanol temperature afforded 0.303 g (96.8%) of 1,1-dimethyl-cis-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (124). The aldehyde was very unstable and could not be purified by chromatography on silica gel, although the reaction appears to contain only one component by nmr spectroscopy. Some purification was achieved by rapid chromatography through a 10 ml column of Florisil¹, eluting with 50:50 ether--hexane: nmr (CCl_4) δ -0.78

¹J. T. Baker trademark for activated magnesium silicate.

(s, 3H), 0.26 (s, 3H), 2.51 (d of d, 1H $J_{DE} = 18$ Hz $J_{DF} = 3$ Hz), 3.04 (d of d, 1H, $J_{DE} = 18$ Hz, $J_{EF} = 2$ Hz), 3.24 (b, 1H), 6.00 (d of d, 1H, $J_{BC} = 7$ Hz, $J_{AC} = 2$ Hz), 6.21 (d of d, 1H, $J_{BC} = 7$ Hz, $J_{AB} = 3$ Hz), 6.80-7.40 (m, 10H), 9.44 (m, 1H); coupling constants were assigned using spin decoupling experiments; ir (film) 3060, 3020, 2960, 2730, 1727 (s), 1680, 1600, 1495, 1295, 1250, 790 cm^{-1} ; mass spectrum (70 eV) m/e 304; mass spectrum calculated for $\text{C}_{20}\text{H}_{22}\text{SiO}$ $m/e = 306.1439$. Found: $m/e = 306.1432 \pm .004$.

Carbon and hydrogen values were found to be nonreproducible and all were below the calculated values. A chemical characterization was therefore carried out using the Tollen's test. A sample of the aldehyde in tetrahydrofuran solution was added to a suspension of excess aqueous silver oxide with stirring for 2 hr, resulting in the formation of a bright silver mirror.

Pyrolysis of exo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-ol (115):

A solution of 0.060 g of the title compound in 1.0 ml of benzene was pyrolyzed as described in the previous experiment. Temperatures were investigated from 275-325°, but none of the aldehyde 124 characterized in the previous experiment could be detected by nmr spectroscopy. The reaction contains numerous products as indicated by the large number of peaks in the silicon methyl region of the nmr.

Acid catalyzed dehydration of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114):

A solution of 0.206 g (0.677 mmol) of the title compound and 0.009 g of *p*-toluenesulfonic acid in 25 ml of dry benzene were heated under reflux for 24 hr using a recirculating Dean-Stark trap filled with molecular sieves. Benzene was removed by rotary evaporation, and the resulting yellow oil was purified by chromatography on a 1.2 x 16 cm column of silica gel, collecting 50 ml fractions.

Fractions 1-4 were eluted with hexane to afford 0.070 g of a yellow oil, which was found to contain three components. The major component was identified as *m*-terphenyl (121) in an overall yield of 23% (nmr yield). Crystallization from pentane afforded pure *m*-terphenyl as white needles, mp 86-87° [lit. (101) mp 87°]. The nmr spectrum shows a multiplet at δ 7.20-7.75 that is identical to an authentic sample.

The second component was separated by liquid-liquid chromatography using a 6 ft by 1/8 in. bondapak C₁₈/porasil B column and acetonitrile--water as carrier solvent and identified as 1,1-dimethyl-2,7-diphenylsilepin (123, 11% (nmr yield). Crystallization from methanol gave needles: mp 60-61°; nmr (CCl₄) δ 0.10 (s, 6H), centers 6.51 and 6.80 (AA'BB' pattern, 4H), 7.10 (d, 10H); ir (CCl₄) 3010, 2990, 1600, 1490, 1440, and 1160 cm⁻¹; mass spectrum (70 eV) m/e (rel intensity) 288 (95), 273 (85), 230 (100), (24 eV) (rel intensity) 288 (100), 273 (10), 230 (10); uv (CH₂Cl₂) λ_{max}

($\epsilon \times 10^{-4}$), 234 nm (1.95), 320 nm (1.10); high resolution mass spectrum calculated for $C_{20}H_{20}$: $m/e = 288.1328$ (corrected for $C^{13}C_{19}^{12}H_{19}Si$ contribution). Found $m/e = 288.1315 \pm .002$.

Anal. Calcd for $C_{20}H_{20}Si$: C, 83.28; H, 6.99; Si, 9.74.
Found: C, 83.25; H, 6.91; Si, 9.96.

The third component was identified as o-terphenyl by comparison with authentic samples on liquid-liquid chromatography (3% overall yield by liquid-liquid).

Fractions 5-8 were combined and concentrated to afford 0.025 g (12.2%) of yellow oil, which was identified as 1,1-dimethyl-cis-2,5-diphenyl-1-silacyclopent-3-ene-2-ethanal (124), by nmr comparison with the sample prepared previously by pyrolysis of the alcohol 114: nmr (CCl_4) δ -0.78 (s, 3H), 0.26 (s, 3H), 2.51 (d of d, 1H), 3.04 (d of d, 1H), 3.24 (b, 1H), 6.00 (d of d, 1H), 6.21 (d of d, 1H), 6.80-7.40 (m, 10H), 9.44 (m, 1H).

Thermal stabilities of o-, m- and p-terphenyl (122), (121) and (137):

A check on product stabilities was carried out by refluxing three individual samples (300 mg) of o-, m-, and p-terphenyl in 25 ml of dry benzene and 0.06 g of p-toluene sulfonic acid. Gas chromatography and melting points revealed that all terphenyls were stable to the reaction conditions under which the bicyclo[3.2.0]alcohol 114 was dehydrated.

Reaction of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114) with trifluoroacetic acid:

To a solution of 0.056 g (0.183 mmol) of the title compound in 0.50 ml of deuterio chloroform was added trifluoroacetic acid dropwise until the nmr spectrum showed no additional change (20 drops). The reaction mixture was diluted with 2 ml of chloroform and washed with a small amount of 10% sodium bicarbonate. The organic layer was dried over anhydrous potassium carbonate and concentrated to a yellow oil. Preparative thin layer chromatography on a 20 x 20 x 0.1 cm plate of silica gel, eluting with 40% ether--hexane afforded 0.015 g (35.4%) of o-terphenyl (122) which was identified by nmr and gc comparison with an authentic sample: nmr (CCl₄) δ 7.05 and 7.30 (s); gc retention time = 2.9 min, 10% SE-30, 1/4 in. by 3 ft column, column temperature = 225°. The reaction mixture shows no trace of m- or p-terphenyl by gc comparison with authentic samples.

endo-1,1-Dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl trifluoroacetate (133):

To a solution of 0.300 g (0.980 mmol) of the endo-diphenyl alcohol 114 in 10 ml of methylene chloride at 0° was added 0.2 ml of trifluoroacetic anhydride and 0.4 ml of trifluoroacetic acid. The reaction mixture was washed with cold sodium bicarbonate solution and cold water. The organic layer was dried over magnesium sulfate and concentrated to a

yellow oil. Residual trifluoroacetic acid was removed by high vacuum pumping to afford 0.386 g (98.0%) of the title compound. The product was used without further purification in subsequent experiments because it was unstable to silica gel chromatography and distillation: nmr (CCl_4) δ -0.13 (s, 3H), 0.40 (s, 3H), 2.50 (m, 2H), 4.15 (d of d, 1H, bridge-head), 5.42 (d of d, 1H, hydroxy methine), 6.72 (d, 1H), 7.00-7.50 (m, 10H); ir (film) 3020, 300°, 1790 (s), 1605, 1500, 1230, 1160 cm^{-1} ; mass spectrum (70 eV) (rel intensity) 402 (1) M^+ , 288 (1), 262 (100) cleavage to silole; high resolution mass spectrum calculated for $\text{C}_{22}\text{H}_{21}\text{F}_3\text{O}_2\text{Si}$ m/e = 402.126266. Found: m/e = 402.124878.

Pyrolysis of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-yl trifluoroacetate (133):

A sample of 0.268 g (0.668 mmol) of the title compound was placed in a vertical Kugelrohr apparatus (0.1 mm) preheated to 250°. The pyrolysis was carried out by successively lowering more bulbs as distillate collected in the outer bulb until three bulbs were inside the oven. The total collected distillate (0.150 g) contained 71.7% (nmr yield) starting material by nmr comparison with an authentic sample. The major product was m-terphenyl (121) (19.9% gc yield) as determined by nmr and gc comparison with authentic samples: nmr (CCl_4) δ 7.50-7.80 (m); gc retention time = 6.4 min, 10% SE-30, 1/4 in. by 3 ft column, column temperature = 225°.

flow rate = 1.7 ml/min. Small amounts (< 5%) of o- and p-terphenyl were also detected by gc, although gc analysis of the starting trifluoroacetate shows m- and p-terphenyl (< 2%).

1,1-Dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl chloride (134):

To a solution of 0.085 g (0.280 mmol) of the endo-diphenyl alcohol 114 in 0.25 ml of deuterio chloroform was added 0.037 g (0.460 mmol) of pyridine and 0.054 g (0.450 mmol) of thionyl chloride in 0.25 ml of deuterio chloroform. The reaction was followed by nmr for 2 hr until no further change could be detected at room temperature. The product was not stable on silica gel or alumina and could be purified only by a rapid column chromatography on 5 ml of silica gel to afford 0.031 g (34.4%) of the title compound as a yellow oil on elution with 5% ether--hexane: nmr (CCl_4) δ -0.11 (s, 3H), 0.40 (s, 3H), 2.80 (m, 2H), 4.05 (m, 1H), 4.72 (d of d, 1H, $J = 7, 8$ Hz), 6.80-7.30 (m, 11H); ir (film) 3000, 1600, 1490, 1450, 1250 cm^{-1} ; mass spectrum (70 eV) m/e 324 M^+ .

A small amount of impurity was removed by dissolving the above oil in hexane and allowing to stand at freezer temperature. The precipitated product was obtained as a tan solid softening 101-103° and was tentatively identified as a rearranged chloride isomer, 1,1-dimethyl-2,7-diphenyl-1-

silabicyclo[4.1.0]hept-3-ene-2-yl chloride (135): nmr (CDCl₃) δ 0.13 (s, 3H), 0.30 (s, 3H), 1.10 (m, 2H), 1.90 (m, 1H), 5.05 (d of d, 1H, $J = 3,8$ Hz), 6.35 (d of d, 1H, $J = 2,8$ Hz), 7.25 (m, 11H); ir (KBr) 1600, 1495, 1255, 830, 705 cm⁻¹; mass spectrum (70 eV) (rel intensity) m/e 326 (11), 324 (30) M⁺, 288 (81), 273 (100); mass spectrum calculated for C₂₀H₂₁ClS; $m/e = 324.1101$. Found: $m/e = 324.1098 \pm .003$.

Dehydrohalogenation of 1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-yl chloride (134):

A solution of 0.099 g (0.335 mmol) of the title compound and 0.057 g (0.335 mmol) of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in 4 ml of acetonitrile was heated at 60° for 12 hr. Solvent was removed by rotary evaporation, and the residual oil was purified by column chromatography on 10 ml of silica gel. Elution with 100% hexane afforded 0.008 g (11.4%) of white solid identified as p-terphenyl by gc and ir comparison with an authentic sample: gc retention time = 6.0 min, 10% SE-30, 1/4 in. by 3 ft column, column temperature = 225°, flow rate = 1.7 ml/min; ir (KBr) 1600, 1500, 1450, 830, 740, 700 cm⁻¹. There was no evidence for o- or m-terphenyl by gc analysis.

Low temperature nmr studies of endo-1,1-dimethyl-2,7-diphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (114) in strong acid media:

A solution of fluorosulfonic acid and sulfuryl chloride fluoride (1:4 v/v) in d₂-methylene chloride was prepared at liquid nitrogen--ether temperatures. A solution of 0.030 g

(0.10 mmol) of the title compound in d_2 -methylene chloride was added and briefly stirred keeping the solution below -120° . The resulting purple solution was stored for several weeks at liquid nitrogen temperatures before spectra were obtained.

The sample was rapidly transferred to a probe pre-cooled to -120° of the Varian HA-100 nmr, but only broad line spectra of the aromatic region could be obtained. On warming to -90° the following nmr spectrum was obtained using fluoro-sulfonic acid as an internal standard: nmr δ 0.58 (s, 3H), 0.72 (s, 3H), 2.50 (b, 1H), 3.50-3.70 (b, 2H), 6.90-8.20 (m, 11H), 9.62 (b, 1H ?).

On warming to -70° the intensity of the silicon methyl signals decreased while a new signal increased at δ 0.92. Continued warming resulted in complete sample decomposition.

endo- and exo-1,1-Dimethyl-2,5,7-triphenyl-1-silabicyclo-[3.2.0]hept-2-ene-5-ol (141) and (118):

A solution of 7.5 ml of 1.0 M phenyl magnesium bromide in ether was added to a solution of 1.52 g (5.0 mmol) of the sila-ketone 110 in 100 ml of ether under nitrogen and refluxed for 12 hr.

Saturated ammonium chloride was added to the reaction mixture at 0° until a sticky white precipitate had formed. The ether solution was dried over anhydrous magnesium sulfate and concentrated to a yellow oil. Chromatography on a 4 x 45

cm column (100 g) of silica gel separated two major components on elution with 5% ether--hexane. Fractions 27-37 (50 ml fractions) were collected and found to contain a mixture of endo and exo isomers of the title compound. A small amount of the endo-alcohol 141 was obtained for characterization by careful recrystallizations from methanol as white prisms: mp 106-108°; nmr (CCl_4) δ -0.20 (s, 3H), 0.64 (s, 3H), 2.12 (s, 1H, exchange with D_2O), 3.05 (s, 2H), 4.14 (d, 1H, \underline{J} = 5 Hz, bridgehead), 6.98-7.60 (m, 16H, aromatic and olefinic); ir (KBr) 3600, 3500, 1600, 1495, 1450, 1255 cm^{-1} ; mass spectrum (70 eV) (rel intensity) m/e 382 (4) M^+ , 262 (100).

Anal. Calcd for $\text{C}_{26}\text{H}_{26}\text{OSi}$: C, 81.63; H, 6.85. Found: C, 81.51; H, 6.99.

Fractions 38-60 were combined and concentrated to afford 0.824 g (43.4%) of a sticky white solid. Recrystallization from methanol gave fine white needles: mp 125-128°; nmr (CCl_4) δ -0.18 (s, 3H), 0.36 (s, 3H), 2.20 (b, 1H, exchanges with D_2O), 2.33 (d of d, 1H, $\underline{J}_{\text{AB}}$ = 12 Hz, $\underline{J}_{\text{BC}}$ = 3.0 Hz), 3.28 (d, 1H, $\underline{J}_{\text{AB}}$ = 12 Hz), 3.73 (apparent t, 1H, $\underline{J}_{\text{BC}}$ = 3.0 Hz, $\underline{J}_{\text{CD}}$ = 12 Hz, bridgehead), 6.15 (d, 1H, $\underline{J}_{\text{CD}}$ = 12 Hz), 6.88-7.30 (m, 15H) (coupling constants were assigned using spin-decoupling experiments summarized in Table 4); ir (KBr) 3520, 2460, 1600, 1590, 1500, 1450 cm^{-1} ; mass spectrum (70 eV) m/e (rel intensity) 382 (4) M^+ , 262 (100).

Anal. Calcd for $C_{26}H_{26}OSi$: C, 81.63; H, 6.85. Found: C, 81.75; H, 6.94.

Acid catalyzed dehydration of exo-1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hept-2-ene-5-ol (118):

A solution of 0.164 g (0.428 mmol) of the title compound and 0.025 g of *p*-toluenesulfonic acid in 25 ml of dry benzene was refluxed for 12 hr using a recirculating Dean-Stark trap filled with 4A molecular sieves. Solvent was removed by rotary evaporation, and the residual yellow oil was chromatographed on 10 ml of silica gel eluting with 5% ether--hexane. Crystallization from methanol gave 0.076 g (57.6%) of white crystals identified as 1,2,4-triphenylbenzene: mp 94-96° [lit. (102) mp 98-100°]; nmr ($CDCl_3$) δ 7.06 (s), 7.06-7.50 (m); uv (methylcyclohexane) λ_{max} = 250 nm, $\log \epsilon$ = 4.39 [lit. (102) λ_{max} = 248 nm, $\log \epsilon$ = 4.54]; mass spectrum (70 eV) m/e (rel intensity) 306 (69) M^+ , 77 (100).

1,1-Dimethyl-2,5,7-triphenyl-1-silabicyclo[3.2.0]hepta-2,5-diene (147):

To a solution of 0.238 g (0.625 mmol) of exo alcohol in 10 ml of methylene chloride was added 0.083 g (1.05 mmol) of pyridine in 1 ml of methylene chloride followed by 0.120 g (0.985 mmol) of thionyl chloride in 1 ml of methylene chloride. The reaction was refluxed for 4 hr; the solvent was removed by rotary evaporation, and the crude chlorides dehydrohalogenated without further purification.

The residual oil was dissolved in 2 ml of deuterio acetonitrile, treated with 0.190 g (1.25 mmol) of 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in 0.5 ml of deuterio acetonitrile, and heated at 50° for 4 hr until the nmr spectrum showed no further reaction. Column chromatography on 6 ml of Florisil¹ separated 0.098 g (59.2%) of the title compound on elution with 10% ether--hexane as a yellow oil. Crystallization from methanol afforded needles: mp. 106-9°; nmr (CCl₄) δ 0.00 (s, 3H), 0.36 (s, 3H), 4.15 (d, 1H, J = 4 Hz), 6.70 (s, 1H), 6.90-7.40 (m, 16H); mass spectrum (70 eV) m/e (rel intensity) 364 (100) M⁺, 349 (74), 306 (50).

Anal. Calcd for C₂₆H₂₄Si: C, 85.66; H, 6.64; Si, 7.70. Found: C, 85.70; H, 6.66; Si, 7.67.

Thermolysis of 1,1-dimethyl-2,5,7-triphenyl-1-silabicyclo-[3.2.0]hepta-2,5-diene (147):

A solution of 0.031 g of the title compound in 0.5 ml of deuterobenzene was heated in a closed nmr tube at 80° for 18 hr. The nmr spectrum shows no change from the starting material.

¹J. T. Baker trademark for activated magnesium silicate.

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ACKNOWLEDGMENTS

I wish to thank Dr. Thomas J. Barton for his advice, encouragement and support during my graduate career. His enthusiasm and devotion to science have made an impression on me that always will be remembered.

Fellow graduate students in the group have contributed many valuable ideas and suggestions to these research efforts. I am grateful for their advice and friendship.

My parents are acknowledged for their support during my education. Their love and understanding helped make this work possible.

I would also like to thank Gulf Oil for their support through the Gulf Oil Fellowship (1971-1972) and Iowa State University, College of Science and Humanities, for a research grant to investigate sulfenium ions.

Finally, I wish to give due credit to my wife, Nancy, for her patience and aid throughout my graduate career. This thesis would not have been possible without her.

I am also indebted to Mr. Louis Sartori for his excellent work on the liquid-liquid chromatography separations.